CR-128505

TO IMPROVE THE FLAME RESISTANCE OF SPANDEX ELASTIC ELASTOMERIC FIBER

report to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

JULY 1972

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Arthur D. Little, Inc.

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I

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We express our appreciation to NASA Houston, Crew Systems Division, for sponsoring the program. Specifically, we want to thank Dr. Frederic Dawn for his technical contribution in monitoring our progress and suggesting new approaches; and T. Ballentine, T. Roderiques and D. Sauers for their assistance in physical property and flammability testing; and Mr. M. Duncan for processing and correlating data on the products.

ABSTRACT

During the second year, our efforts centered around improving the strength characteristics of fibers to pass the 70% oxygen/30% nitrogen specification; developing spinning techniques; and developing information about incorporating these fibers in fabric structures using wrapping materials of Beta Fiberglas, Nomex and PBI.

We have worked with formulations based on urethanes, fluorinated polymers, and combinations of the two. Each formulation included flame-retardant additive. We have shown that urethane is so flammable that up to 90% additive must be incorporated to get the necessary flame-retardant properties. At this level, tensile strength drops to an unacceptable level of less than 500 psi. For this reason, we devoted our efforts to the fluorinated polymers which are inherently more flame retardant. The best of these polymers was Viton. Our best formulation at present is based on 100 parts of Viton, 100 parts of decabromobiphenyl (flame retardant) and 7 parts of plasticizer (phosphate) and curing ingredients.

These formulations can be either wet spun or melt spun to fibers that have a tensile strength of 1300 to 1500 psi and an elongation of 450%. However, the melt spinning procedure is the easiest to handle and, therefore, the preferred method. Special techniques were developed for extruding the uncured fiber into filaments and cooling to prevent sticking prior to and during the curing process. The process currently produces 12 individual monofilaments at one time at a capacity of 5-7 pounds per day. If necessary, the production rate can be increased by scaling up the equipment.

Power net fabrics made with this fiber can be made equal in power and elongation to spandex in structures by using a fiber somewhat heavier than regular spandex.

Structures have been prepared using various knitting techniques, including power net from fibers wrapped or braided with PBI, Nomex and Beta Fiberglas. The uncovered elastomeric fiber has also been knit into the different nonelastomeric fibers. The handling of any new elastomeric fiber, however, requires the knitter to become acquainted with its stretch and handling characteristics on the machine; the techniques need to be perfected.

One of the major problems has been to determine the best nonelastomeric fiber. Each of the three candidates -- fiberglass, Nomex and PBI -- has its advantages and drawbacks. The Beta Fiberglas is completely flame resistant and may be used in a variety of applications under static conditions. Nomex has excellent properties and feel, but will burn in the 70% oxygen/30% nitrogen atmosphere unless it is treated. Monsanto's treatment, however, entails high temperatures that completely destroy the elastomer fiber. Hooker's treatment, now in the development stage, avoids the use of high temperature, but the finish is not

washing. PBI currently is the most promising covering fiber, since the finished fabric or skein of yarn can be treated without affecting the elastomeric fiber. The problem in using PBI is the availability of multifilament of less than 200 denier. However, 50 filament yarns, which are equivalent to 100 denier, show promise in power net structures.

At present, the following additional steps are required to optimize the products:

1. Improve the elastomeric fiber to alter the character of the smoke that is produced when the fabric is first ignited. In the 30 seconds the igniter is on, acrid, irritating, black smoke is produced.

2. Improve the power knit of the fibers so they will approach as nearly as possible that of regular spandex.

3. Thoroughly test the fiber in a variety of environments to determine those that will cause deterioration. It has been shown, however, that the fiber has excellent chemical characteristics and good solvent resistance, and good high-temperature resistance, although exact degrees of resistance have not been determined.

4. Finalize on the optimum fabric structures with respect to type of power net that should be used and the type and size of covering fibers.

5. Work with the knitters and companies that provide covering fiber treatment on the techniques of handling the fiber and treating the covering fibers for flame retardancy either before or after knitting.

I. INTRODUCTION

In space exploration, nonflammable elastomeric fabrics are required in space suit systems, crew equipment, and various applications in the spacecraft where a material with a high elastic memory is required -- for example, a liquid-cooling garment, a sleep-monitoring cap, elastic tie cords, and sleep-restraint systems.

Under Contract NAS 9-10424, a number of urethane polymer systems were synthesized -- many with better flame-resistant properties than spandex. In addition, many compositions based on fluorinated and urethane polymers and organic additives, were prepared and met nonflammability specifications. A number of these compositions that were self-extinguishing in the 70% oxygen, 30% nitrogen atmosphere were spun into fibers and incorporated into fabric structures of various designs. These have been successfully power knit with nonelastic PBI, Nomex and Beta Fiberglas to give nonflammable elastomeric structures that do not burn in a 70% oxygen, 30% nitrogen atmosphere.

Although this program substantially advanced the state-of-the-art, additional improvements can be made. For example, the compound composition could be modified to provide greater strength; spinning techniques, methods of wrapping fibers, and methods of knitting fabric structures could be improved. The final product could be tested in more detail to determine what chemical and physical environments may adversely affect the structures.

II. BACKGROUND

In the program for 1970-1971, which is covered in our report dated March 1971, various urethane-type polymers were synthesized, and many had better flame resistance than spandex. The most efficient means of producing flameproof fibers, however, was by incorporating halogenated additives into urethane or fluorocarbon elastomers. Some of the resultant fibers were not flammable even in a 100% oxygen environment.

Various flexible polyurethane structures containing halogen were synthesized from polyesters derived from aliphatic or aromatic polyols and dibasic acids. Aliphatic halide structures could not be used because they are unstable at the required reaction temperatures, giving off hydrogen halide which hydrolyzes the ester linkages. In contrast, halogen-containing aromatic polyols are stable and satisfactory products were made.

The most promising composition, a brominated neopentyl glycol capped with toluene diisocyanate, was used as a conventional diisocyanate, in conjunction with hydroxy-terminated polyethers or polyesters to form elastomeric urethanes containing about 10% bromine by weight. Products made in this manner will not burn in air, have an oxygen index value of about 25, and have tensile strength values of about 5000 psi at 450% elongation.

The most efficient additives for imparting flame retardancy to spandex urethanes are aromatic halides and the most effective of these are the bromide compounds. Various levels of flame retardancy were achieved, depending on the levels of additives used. Compositions were prepared and tested to meet the following specifications:

a. <u>35% Oxygen/65% Nitrogen</u>: These urethane compounds have tensile strengths of 1500-2000 psi and elongations of 300-450%. They contain 20-30% urethane with the remainder flame-retardant additives (hexabromobenzene in combination with trisbromochloropropyl phosphate as a flame-retardant plasticizer).

b. <u>70% Oxygen/30% Nitrogen</u>: These urethane compositions have tensile strength values of 400-900 psi, elongations of 250-400%, and oxygen index values of 75-85. They are composed of about 5% urethane, 20-30% fluorinated polymer, and 65-75% hexabromobenzene/trisbromochloropropyl phosphate.

Although it was possible to achieve the necessary flame retardancy, the physical properties were so inferior that serious problems would be encountered in making fabrics with the necessary recovery and strength characteristics.

This second phase (covered in this Report), carried out in 1971 and early 1972, resulted in improvement of the fibers' physical properties and production of a limited number of fabrics from these elastomers in combination with fiberglass, Nomex and PBI fibers. To achieve these results, we had to evaluate a large variety of flame retardants and additives and prepare a sufficient amount of fabrics to give a preliminary indication of the type of structure that would be required to obtain properties that were nearly equivalent to standard spandex fiber fabrics. During this phase, we prepared both films and fibers as well as knit structures that met the flame-retardancy requirements and had physical properties that approached those of spandex fibers. This we achieved by increasing the weight of elastomeric composition in the fabric.

III. URETHANES

At the completion of the first year's program, we had finalized on two urethane formulations for further modification and eventual use in knitted structures:

1. A compound synthesized by treating brominated neopentyl glycol with TDI and then treating with the polyester of butanediol and adipic acid. This compound had an oxygen index of 25 versus 19 for a regular spandex.

2. A formulation based on a commercially available spandex and the use of additives to impart higher level flame resistance:

Material	Parts By Weight
Spandex urethane	20
Hexabromobenzene	56
Trisbromochloropropyl phosphate	24

A. PROPERTIES AND COMPOUNDING

1. Synthesized Products

Prior to preparing substantial quantities of the polyester urethane from dibromoneopentyl glycol (similar to that reported previously), we prepared a polyether so that we could compare the physical and flame-retardant properties of these two types of structure. Our conclusion is that the polyethers have poorer flame resistance than the polyesters at a given bromine concentration. Structure apparently is the dominating factor. The polyether had a lower oxygen index (24 versus 25) than the polyester despite bromine contents of 17% and 10%, respectively. (Table III-1). Furthermore, the soft (non-urethane) segment is too small, and results in a brittle polymer.

We prepared several batches of the dibromoneopentyl glycol polyester urethane (Table III-1, XM 16717-60), for use in the additive program prior to the preparation of the 15-pound batch and to establish reaction conditions. Each batch exhibited properties very nearly equal to those of pure spandex. The total synthesis requires 12 to 16 hours and involves three main steps:

a. End cap the dibromoneopentyl glycol with TDI. This leaves an excess of NCO groups,

b. Treat the capped glycol with poly (butylene adipate),* and

c. Extend the resulting product with hydrazine.

---

* Witco L8-71

TABLE III-1

PROPERTY DATA FOR URETHANE POLYESTER AND POLYETHER

	XM-16717-53	XM-16717-60
Soft Segment, Type	polyether (1)	polyester (2)
Soft Segment, Chemical Name	poly (THF)	poly (butylene adipate
Soft Segment, Molecular Weight	660	2000
Wt. % Bromine	17	10-11
Oxygen Index	23-24	24-25
Ultimate Tensile Strength, psi	7000	7000
Ultimate Elongation, %	200	500
Elasticity	none	good
Recovery	none	good
Color	water white	water white
Wt. % Soft Segment	35.0	69.6
Wt. % TDI	37.1	12.1
Wt. % SA1138	27.9	18.3

(1) Quaker Oats Polymeg 660

(2) Witco L8-71

We attempted to improve the strength and heat resistance of highly loaded urethane systems and to increase the tensile strength of the wet-spun fiber by incorporating some XM-60 prepolymer (NCO terminated) into the spinning dope. The improvements, we thought, would come from cross-linking via the NCO group. To this end, we prepared spinning dope that contained 20% spandex and 80% additive on a dry-weight basis and investigated the effect of prepolymer at two concentrations:

- concentration equal to spandex (urethane) content, and
- concentration 50% of spandex content.

Immediately after the prepolymer was mixed into the dope, the fibers were wet spun and then cured for two hours under water in a reactor at 80°C and 105-psig nitrogen. At the end of this time, they were removed, dried and the physical properties determined. No significant differences could be found.

Since allophanate cross-linking of urethanes is known to yield stronger products, we cast films of the XM-60 prepolymer and dried them overnight. The resulting films were very tough, with tensile strengths of 7000 to 8000 psi, and had very good elasticity and recovery.** With this technique, prepolymers of much lower viscosity can be used--thus raising the possibility of using a dry (non-solvent containing) spinning procedure. For example, dry spinning might be used with 1,4-butanediol as a cross-linking agent--mainly through the urethane's NCO linkages--to effect a rapid cure.

Since the basic requirement of the contract was to produce an elastic elastomeric fiber that would not burn in a 70% oxygen/30% nitrogen atmosphere, we analyzed the strength and flammability characteristics of the various systems that we had developed. Table III-2 and Figure III-1 summarize the relative physical and flame-retardant properties of the most promising elastomeric formulations.

In cast film form, 20% spandex, 20% XM-60 and Viton formulations show good flame resistance and reasonable tensile strengths. Of the three, the 20% spandex film has the best tensile strength, although the lowest flame resistance. For applications requiring high flame resistance, the Viton formulation was the best. The XM-60 formulation is superior to the others only in tear resistance. Since high tear srength is not a prerequisite for a good elastomeric fiber, this formulation does not provide any desirable fiber properties that cannot be obtained with either the spandex or the Viton systems. Therefore, we see no advantage in using the XM-60 formulation product.

** These films recover somewhat better than the standard hydrazine-extended, linear urethane films.

TABLE III-2

PROPERTIES OF CAST FILMS OF CANDIDATE FORMULATIONS

Material	Spandex	XM-60 (1)	20% Spandex 80% HBB (2)/T-23P (3)*	20% XM-60 80% HBB/T-23P	Viton A/HBB/T-23P**	Later Modifications***
Property						
Tensile Strength, psi	-	3530	1047	487	404	1500
Elongation, %	-	641	630	275	500	450
Tear Resistance	-	1.37	0.61	1.77	0.6	-
Propagation Rate at 70% O_2-30% N_2, in/sec	1.33	0.833	-	0.20	0.11	S.E. in 1 7/8 in.
Oxygen Index	19	25	45	55	100	100

(1) XM-60 - urethane based on dibromoneopentyl glycol

(2) HBB - hexabromobenzene

(3) T-23P - tris (dibromopropyl) phosphate

* HBB/T-23P in the ratio of 56/24

** Viton A/HBB/T-23P in the ratio of 100/200/30

*** Viton B/DBBP/TCP 100/100/10

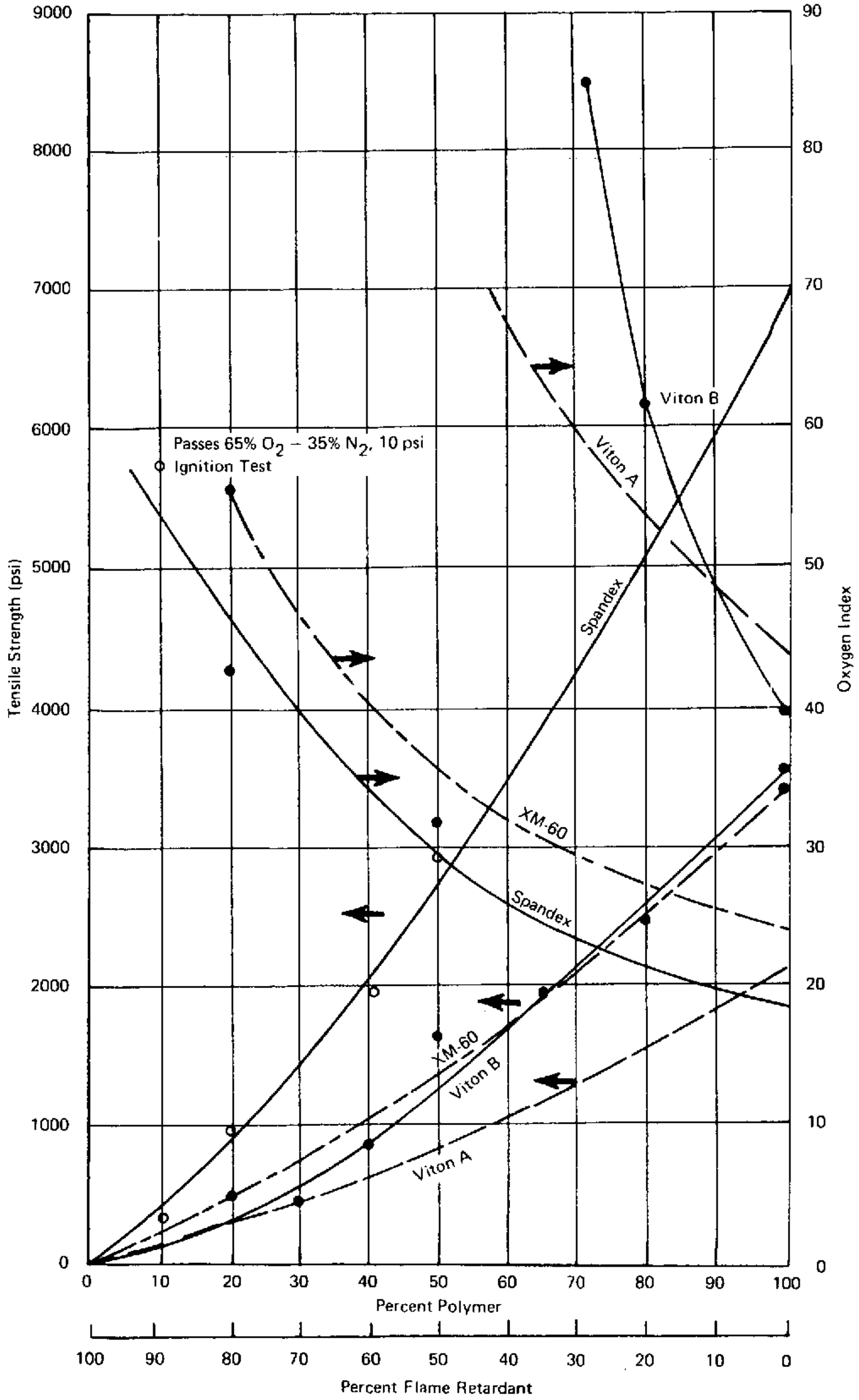


FIGURE III–1 EFFECT OF FLAME RETARDANT ON TENSILE STRENGTH

For example, if the elastomeric fiber must have a tensile strength of 2000 psi, the Viton formulations will give this strength and provide superior flame resistance:

Material	Spandex	XM-60	Viton A	Viton B*
% Polymer	38	66	95	67
Oxygen Index	35	30	45	85

Viton A cannot be used for applications that require a tensile strength greater than 2200 psi, but for a tensile strength of 2500 psi, for example, Viton B or even spandex would give the required tensile and better flame resistance than the XM-60:

Material	Spandex	XM-60	Viton A	Viton B*
% Polymer	45	80	-	80
Oxygen Index	32	28	-	63

In general urethanes are best for applications that require very high tensile strengths and only a minimum flame resistance. Although the Viton B modified formulation is a later development, it is mentioned here because it has a bearing on the decision to work entirely with Viton B.

The relatively low tensile strength of the tested batch of XM-60 (compared to that of spandex) makes the brominated polymer appear unsatisfactory for the described applications. However, we found some batch-to-batch variation with the XM-60 formulation. At one time we obtained an ultimate tensile strength of 7000 psi, whereas, in the present case, we measured the ultimate tensile strength at only 3350 psi.

A number of synthesis pathways are open that might improve the physical properties of the XM-60 polymer. For example, a symmetric diisocyanate, MDI, might be used in place of the asymmetric TDI. This symmetry will increase the polymer tendency to form reinforcing crystallites and a higher tensile strength will result. Alternatively, cross-links may be introduced into the polymer to take up some of the load-bearing requirements. Cross-links may be produced through the use of trimethylol propane, glycerine or pentaerythritol in the chain extension reactions. Another possibility is to fractionate the polymer and select only the high-molecular-weight fragments. However, we felt that continued work on this system was not warranted at this time and that more fruitful results would be obtained from other systems. Therefore, we directed our efforts toward improving the spandex and Viton formulations and toward developing optimum techniques for producing fibers from these formulations.

---

* New formulation described later on in Report

2. Spandex Additive Program

The major effort on the spandex with additives was concerned with process improvement so that substantial amounts of the product could be produced. The basic formulation developed during the previous contract was used as a starting point for modification:

Material	Parts By Weight
Spandex urethane	20
Hexabromobenzene	56
Trisbromochloropropyl phosphate	24

This formulation appeared to be satisfactory when the product was tested in a 70% oxygen/30% nitrogen atmosphere by the Limiting Oxygen Index (LOI) method. However, it would not pass NASA's silicone igniter test at this level. In order to pass, it was necessary to increase the flame retardant to about a 90% level and at this point the physical properties were degraded to such an extent that the product was completely unacceptable. Attempts to substitute other additives were not successful, because of a variety of problems. Briefly, the systems tried and the problems encountered were as follows:

a. The brominated urethane synthesized at ADL was incorporated into the regular spandex formulation, as described previously. At any given flame-retardancy level, the combination was not stronger than the spandex additive formulation.

b. During our 1970 program, we conducted some preliminary work to evaluate the possibility of using elastomers as flame-retardant additives to urethane. This work was continued and other halogenated rubbers investigated as additives. The oxygen index values of these rubbers without additive and with 50% hexabromobenzene are shown in Table III-3. Attempts to incorporate these elastomers with the urethane spandex formulations presented problems because they were incompatible or could not be dissolved in mutual solvents for spinning.

B. FIBER SPINNING

The wet spinning of urethane fiber was covered in our first report, but the process has since been changed to improve the efficiency.

The basic process steps remain the same. The urethane is dissolved in DMF at 15% solids, the flame-retardant materials added, and the combination ball milled overnight. The composition is then de-aerated and filtered. The spinning dope, also containing flame retardant, is pumped through a spinnerette with a positive displacement pump and dropped into a water bath to precipitate the fiber and

TABLE III-3

OXYGEN INDEX VALUES

Material	No Additive	With 50% Hexabromo Benzene
Viton A	48	75
Hypalon 20	26	42
Neoprene W	27	55

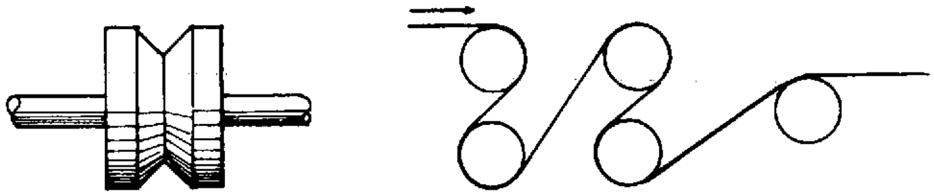
eliminate the solvent. Forty ends are passed through V-shaped rolls that coalesce the fibers and remove excess water. Within these basic steps, however, a number of design changes have been incorporated to allow for the fact that our formulation must be a heavy denier because of its low power (strength) and that trapped air carried in with the filler must be removed. Significant changes were made in the rolls for the bath and in the take-up rolls between the bath and oven. For example, the nylon rolls in the bath were widened and positioned one directly underneath the other (Figure III-2). This change resulted in more of the solvent being removed in the bath before the fiber entered the oven. These changes have resulted in better coalescence of the fibers. Other changes include the addition of fans to the oven to provide better air circulation, and the use of two spinnerettes that provide 100 ends of the same diameter rather than 40. The spinnerette change permits a heavy denier fiber to be prepared.

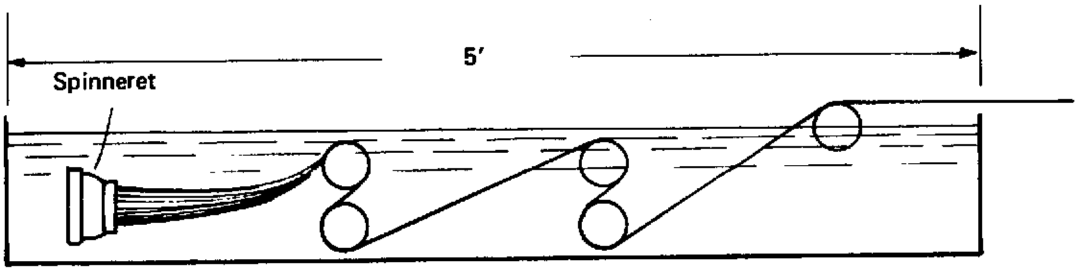
Figure III-3 shows photographs of fiber which was spun after these equipment modifications had been made. Figure III-4, included for comparison, shows the structure of the fiber before these modifications and the appearance of an unmodified spandex fiber. The formulation used was our standard preparation:

Material	Parts by Weight
Spandex	20
Hexabromobenzene	56
Trisbromochloropropyl phosphate in DMF	24
N,N-dimethylformamide	170

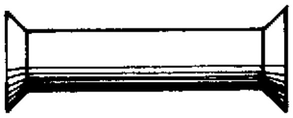
Once the fiber comes out of the bath, it passes through a series of V-shaped grooved pulleys arranged to squeeze excess water out of the fibers.

The fiber prepared in the modified equipment varied in thickness from 15 to 19 mils, which is equivalent to a 930- and 1500-denier spandex, respectively. Because of their bromine content, the density of these fibers is three times that of the spandex. Elongation is about the same as that of the spandex. However, this fiber lacked both the strength and flame resistance to be considered as a candidate to meet the specification. Power is about 1/7 and oxygen index is about 50. Therefore, we further refined the process, using the following 28% solids formulation for our tests:



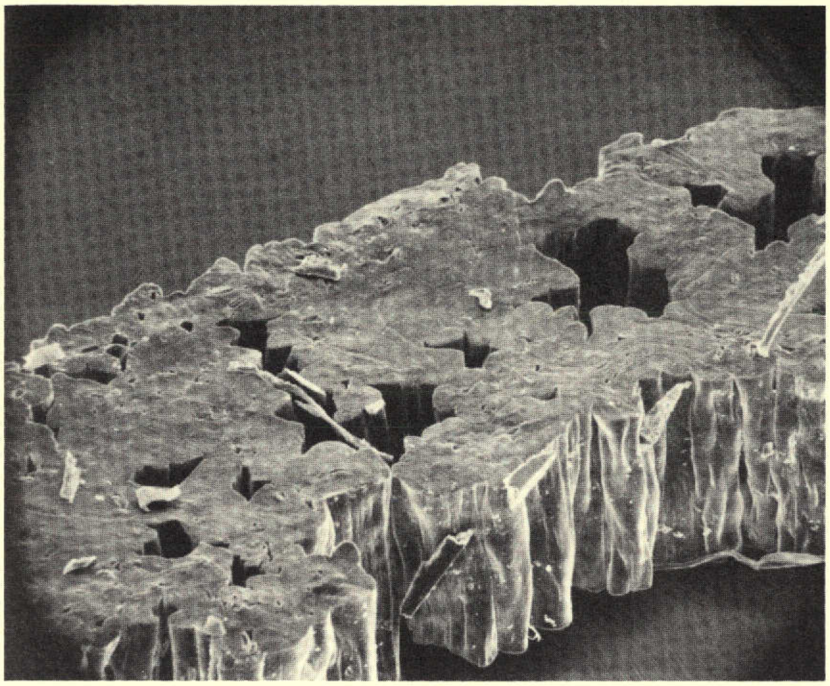


Bath Design

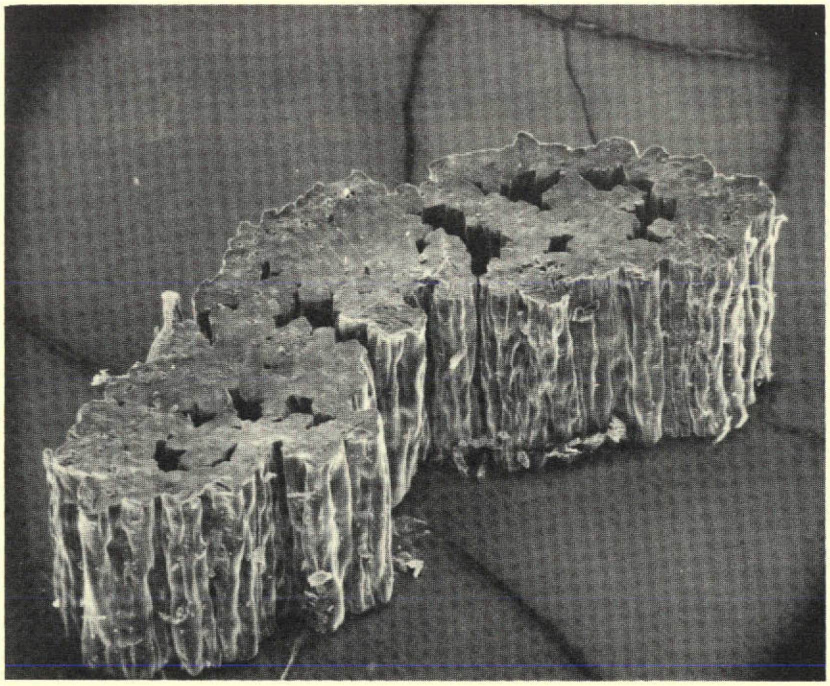


Bath Roll Design

FIGURE III-2 SQUEEZE ROLLS

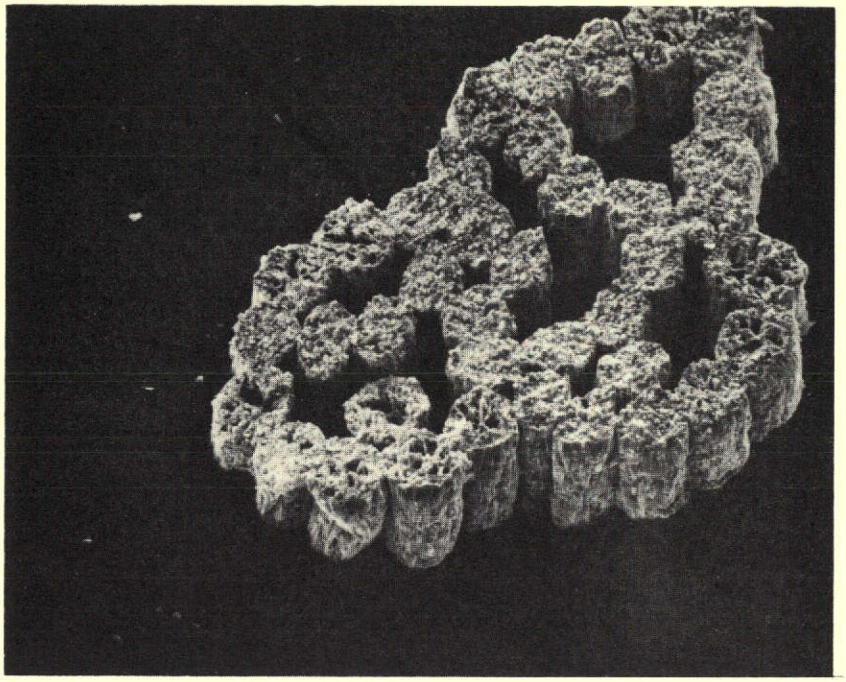


200X Magnification

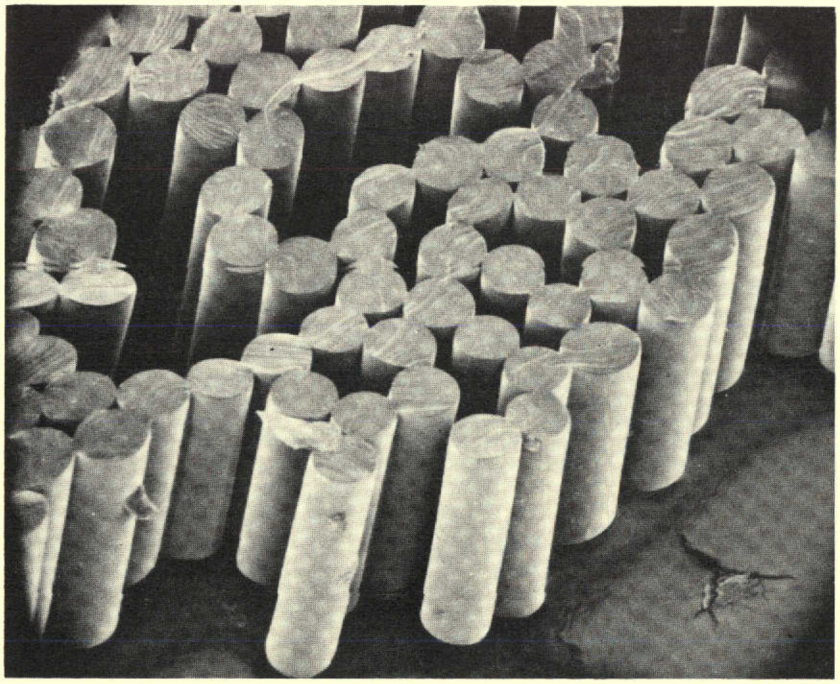


100X Magnification

FIGURE III-3 MODIFIED FLAME RESISTANT SPANDEX



A. Modified Spandex



B. Unmodified Spandex

FIGURE III-4 CROSS-SECTIONAL VIEW OF FIBER DRAWN THROUGH 40-END SPINNERETTE

Material	Parts by Weight
DMF	71.5
Hexabromobenzene (Michigan Chemical)	20
Spandex (duPont Lycra)	8.5

After it was ball milled for 16 hours, de-aerated and filtered through cheesecloth, this solution was pumped through a spinning head that contained forty 0.012-inch diameter holes. The 40 filaments so produced were coagulated in a water trough and and drawn together into a single multifilament fiber. This fiber was then passed through a drying tunnel to the take-up reel.

The last traces of solvent were removed from the fiber by placing the entire take-up reel in a forced convection oven at 100°C for 16 hours. The properties of the dried fiber, which consisted of 70% hexabromobenzene and 30% spandex, are given in Table III-4.

TABLE III-4

PROPERTIES OF SPANDEX FIBERS - FIRST TRIAL

Fiber Characteristics		Width	Thickness
Filament Diameter:	0.005 in.		
Fiber Dimensions:	ribbon	0.040 in.	0.007 in.
Physical Properties			
Tensile Strength:	700-1400 psi		
Elongation at Break:	250%		

The values for tensile strength and elongation were considerably below the theoretically obtainable values, and scanning electron photomicrographs were taken of the fiber cross-section to ascertain the reason.

Figure III-5 shows the substantial porosity of these fibers. This porosity explains the low tensile strength, since tensile is based on the cross-sectional area defined by the outside dimensions of the fiber. The porosity, and possibly the presence of small amounts of solvent, also explains the relatively low elongation at break.

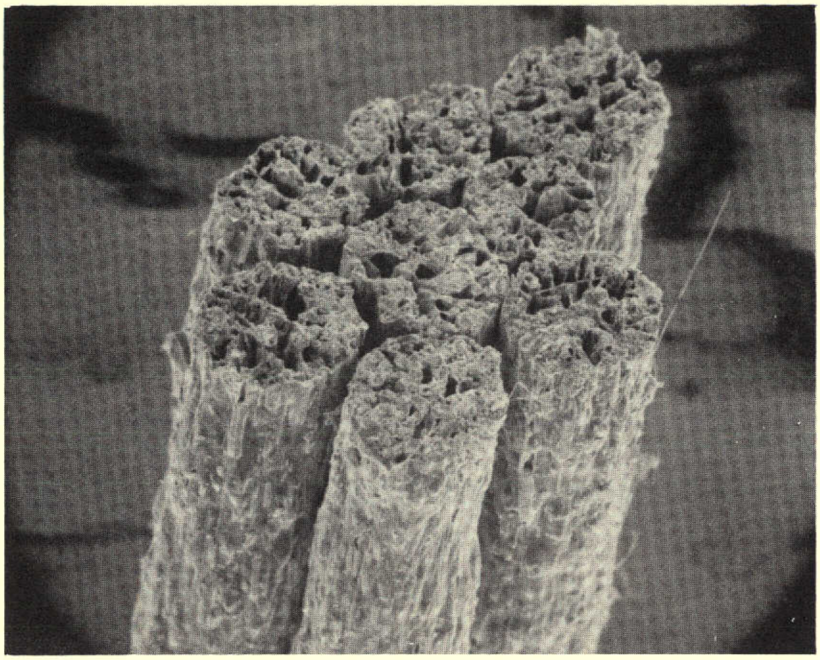


FIGURE III-5

POROUS SPANDEX FIBER

200X

FIGURE III-6

POROUS FIBERS

2000X

Note Hexabromobenzene Particles

Voids tend to form in fibers when solvent and water become trapped within a coagulated and "set" fiber sheath. A sheath or skin forms--because solvent is removed from the fiber surface more rapidly than solvent can diffuse from the innermost sections--and this sheath prevents the fiber from coalescing during the drying operations. Consequently, the fiber retains its "as spun" dimensions while the solvent and water are removed and voids are produced.

A number of factors control the porosity of the fiber:

(1) Filament Diameter in the Coagulation Bath: The filament diameter should be fine enough to permit the filament to rapidly equilibrate with the bath conditions and produce a homogeneous cross-sectional composition. If too large a diameter is spun, the skin of the filament will set before most of the solvent has had time to diffuse out. If too small a diameter is spun, the resulting multifilament fiber will not have sufficient strength to be drawn from the bath without breaking.

(2) Temperature of the Bath: The bath temperature controls the diffusion rates of solvent and water. High bath temperatures result in skin formation because the heat penetrates the filaments from the outside in--increasing the diffusion rate of the solvent in the outer layers of the filaments first.

(3) Composition of the Bath: The coagulating bath should contain a mixture of nonsolvent and solvent to slow the rate at which solvent is removed from the filament surface until this rate matches the rate of diffusion of solvent within the filament.

(4) Concentration of the Spinning Solution: The percent solids of the spinning solution determines how much solvent has to be removed to coagulate the filaments. A low percent solids is conducive to slow coagulation of the filaments and a more uniform filament.

The tensile strength of the fiber, in addition to being a function of porosity, is also a function of the particle size of the hexabromobenzene filler. The gross nature of the filler is illustrated in Figure III-6. The filler particles in this illustration are 2-4μ in diameter. Ideally, for optimum tensile strength, the particle size should be less than 1μ. To achieve this, the filler must be air-mill ground before it is incorporated into the formulation. A comparison of the unground, ball-mill ground, and air-mill ground hexabromobenzene can be obtained by examining Figures III-7, -8 and -9.

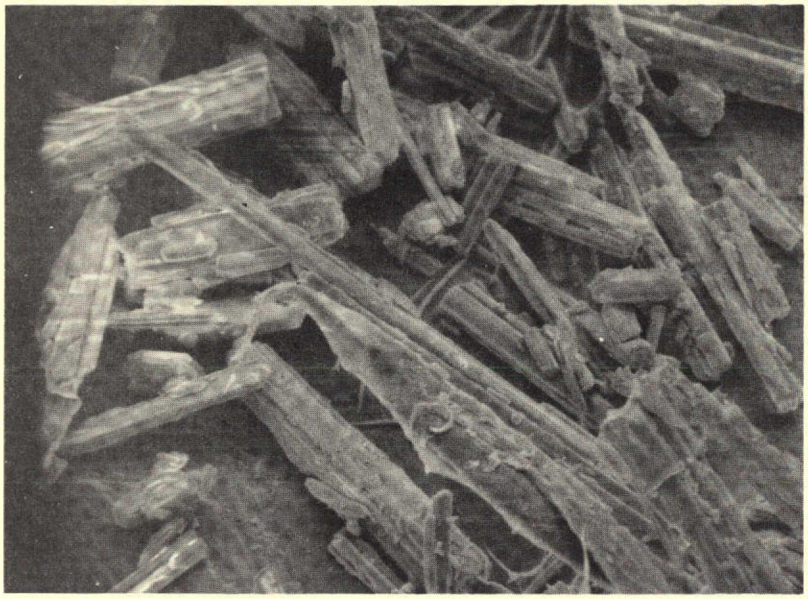


FIGURE III-7

HEXABROMOBENZENE

UNGROUND

1000X

(Average length of

particles is 150μ)

FIGURE III-8

HEXABROMOBENZENE

BALL MILLED

16 hours

600X

(Particle size 2 - 10μ)

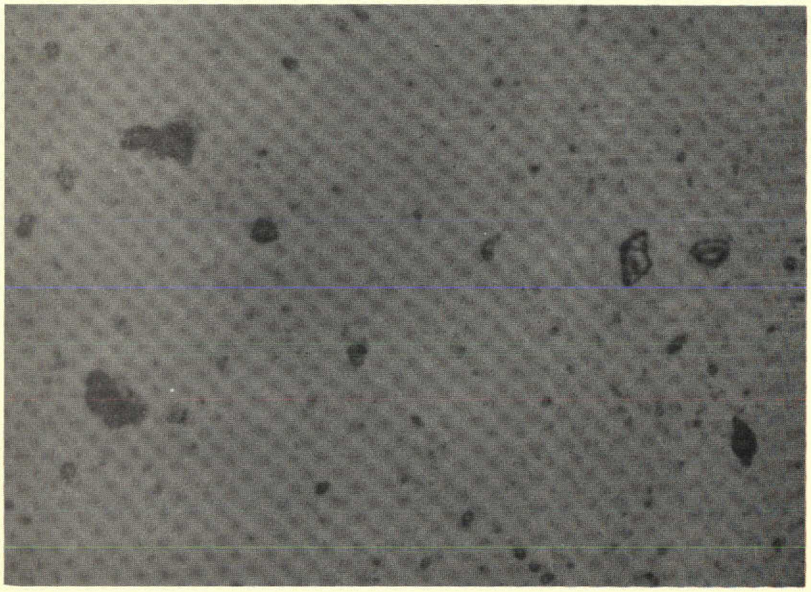


FIGURE III-9

HEXABROMOBENZENE

AIR-MILL GROUND

600X

(Particle size for

most particles <0.5μ)

On the basis of the foregoing analysis, the spinning conditions were changed as shown in Table III-5.

TABLE III-5

CHANGES IN SPINNING CONDITIONS

	Initial Conditions	New Conditions
Spinning Head	0.012-inch diameter holes (40)	0.008-inch diameter holes (40)
Bath Composition	100% water	40% DMF, 60% water
Bath Temperature	130°F	68°F
Filament Diameter	0.005 inch	0.0012 inch
Spinning Solution	28% solids	20% solids
Filler Particle Size	2-4μ hexabromobenzene	$<$0.5μ hexabromobenzene
Oxygen Index	45	45

The physical properties of the fiber spun under these new conditions were:

- tensile strength: 2000-2500 psi
- elongation: ~475%

A scanning electron photomicrograph of the cross-section of this fiber is shown in Figure III-10. Note, in particular, the low porosity and fine filler particle size.

About 5000 feet of this fiber were spun in deniers ranging from 180 to 210. This size was selected to duplicate the spandex construction of an open, lightweight warp knit structure chosen by NASA for use in sleep-restraint systems and instrumented head caps.

C. PHYSICAL PROPERTIES AGING TESTS

The use requirements of the flame-resistant spandex fibers under development require that the products be stable under a variety of conditions. Halogen-containing polymers are normally protected by the use of a metal salt that reacts with any hydrogen halide present as a result of depolymerization. Samples were prepared for ultraviolet light and heat stability tests. The formulations and results are shown in Table III-6 for ultraviolet light and III-7 for heat stability.

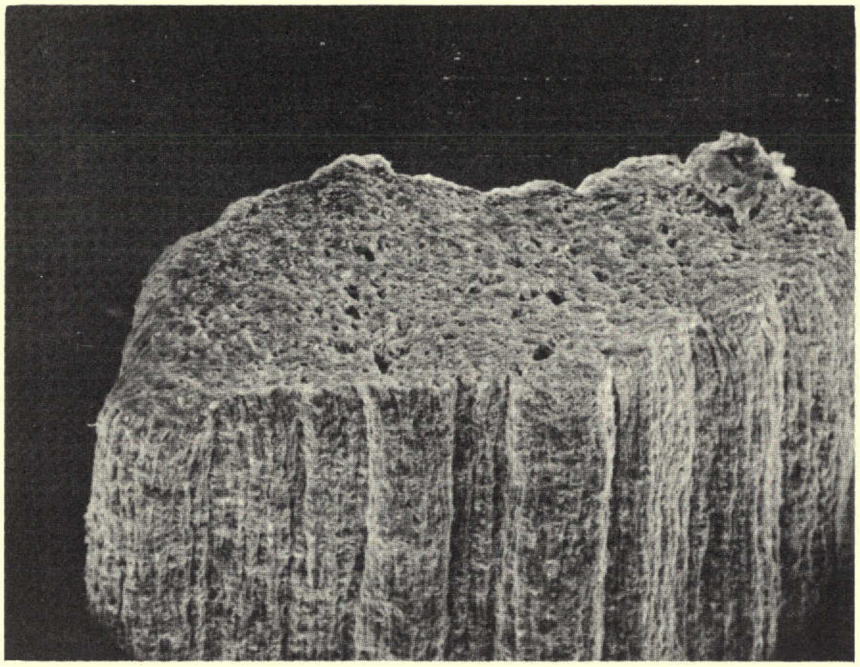


FIGURE III-10 **SPANDEX FIBER** 450X

Note Filament Coalescence

TABLE III-6

ACCELERATED AGING TESTS OF SELECTED CAST FILMS

			Comments		
	Materials	Parts by Weight	Exposed 1 day	Exposed 3 days	Exposed 3 weeks
1.	Spandex	100		good strength, elastic film	
2.	Spandex	100			
	Mark WS *	1.5			
	Mark 202A **	1.0			
3.	Spandex	20	Sample decomposed		
	HBB	56			
	Tris(bromochloropropyl) Phosphate (T-13P)	24			
4.	Spandex	20			
	HBB	50	poor strength	Sample decomposed	
	T-13P	24			
	Mark WS	1.5			
	Mark 202A	1.0			
5.	Spandex	30		good strength, elastic film	
	HBB	70			
6.	XM-60	100		good strength, elastic film turned brownish color	

* Mark WS - Barium Cadmium stabilizer (Witco Chemical Co.)

** Mark 202A - U.V. absorber (Witco Chemical Co.)

TABLE III-6 (Continued)

ACCELERATED AGING TESTS OF SELECTED CAST FILMS

			Comments		
	Materials	Parts by Weight	Exposed 1 day	Exposed 3 days	Exposed 3 weeks
7.	XM-60	100	good strength, elastic film		
	Mark WS	1.5	turned brownish color		
	Mark 202A	1.0			
8.	XM-60	20	inelastic film, poor strength		
	HBB	56			
	T-23P	24			
9.	XM-60	20	inelastic film, poor strength		
	HBB	56			
	T-23P	24			
	Mark WS	1.5			
	Mark 202A	1.0			

Whenever plasticizers T-23P (tris-1-bromochloropropyl phosphate) or T-13P (tris-2,3-dibromopropyl phosphate) were present in the formulations, the film properties degraded under UV exposure. The incorporation of stabilizing agents into the films had little effect in preventing this degradation. As a result, these plasticizers will not be used in the spandex formulations.

We conducted heat stability tests at 90°C for 24 hours plus four hours at 130°C on regular spandex and the XM-60 formulations. The bromine appears to form a relatively strong bond with the chain and stability should be as good as the regular spandex. A comparison before and after heat aging is shown in Table III-7.

TABLE III-7

THE EFFECT OF HEAT AGING ON PHYSICAL PROPERTIES OF SPANDEX AND XM-60

Property	Regular Spandex	XM-60
Tensile Strength, psi		
Before Heat Aging	8000	6100
After Heat Aging	7400	7000
Elongation, %		
Before Heat Aging	700	800
After Heat Aging	600	500
Oxygen Index		
Before Heat Aging	19-20	25
After Heat Aging	19-20	25
Percent Loss in Weight	0.5	.04

The conclusions that can be drawn from this study are that the synthesized urethane was as stable as regular spandex to these conditions: 90°C for 24 hours plus four hours at 130°F and ultraviolet light. Regular spandex with the hexabromobenzene is not degraded under heat aging at these temperatures. (At high temperatures, 300°F and above, spandex is not particularly stable and hexabromobenzene shows some loss of volatiles.) Decabromobiphenyl, however, is stable and can be used as a direct replacement. (See Section IV.)

At this point in the program, work on the urethanes was discontinued in favor of more work on the Viton formulations.

IV. HALOGENATED POLYMERS

As the program progressed it became apparent that urethane polymers can be made flame retardant, even in atmospheres of 100% oxygen, but the large amounts of additive required degrade the physical properties to a point where they are poorer than those possible with other polymers. For example, a 94% loading of hexabromobenzene is required to achieve an oxygen index of 100, with urethanes and the compounds are brittle and unusable. With Viton, a 50 to 60% loading of hexabromobenzene will give the same oxygen index and reasonably good physical properties.

For this reason, our efforts during this phase of the program were directed chiefly to fluorinated polymers alone or in combination with the urethanes.

The section on properties and compounding covers manufacturing techniques only in instances where problems in processing pointed out a need for change in compound.

A. PROPERTIES AND COMPOUNDING

1. Halogenated Polymers

As part of the program to provide more efficient flame-retardant additives for the urethanes, we evaluated three commercially available chlorinated elastomers: Neoprene W (40.5% Cl). Hydrin 100 (39.5% Cl), and Hypalon 40 (34.5% Cl). We also tested a fluorinated elastomer, Viton A, which has a fluorine content of 76%.

Tables IV-1, IV-2, and IV-3 show the formulations that were prepared, their oxygen index, and physical properties. Each of these polymers was cured alone and with hexabromobenzene additive, and their oxygen index and physical properties were determined.

Since our spinning process required the spandex urethane additives be put into spinning solutions, any additive polymer must have mutual solubility. None of the halogenated rubbers except Viton was soluble in either DMF or MEK--two solvents for urethane. At present, therefore, the polymers cannot be used with urethanes, but could be used by themselves as fibers since they can be spun from solution.

To overcome this solubility problem, we would need to synthesize a low-molecular-weight urethane similar to the XM-60. Such a compound would be soluble in the same solvents that are suitable for the halogenated rubbers. Viton showed considerable promise as an additive to the urethane; with this additive, we were able to formulate systems that will not burn in a 100% oxygen environment. However, since the urethane is very flammable, loadings of flame retardant must be higher than if Viton were used alone. Furthermore, for a 100% oxygen environment, the inclusion of urethane does not enhance the physical properties.

TABLE IV-1

POLYMER EVALUATIONS

Book #	Formulations (Parts by Weight)	Curing Condition (in oven)	% Halogen in Formulation	Oxygen Index	Tensile Strength (psi)	Elongation (%)
36-C	Viton A 100 Lead Oxide 15 Diak #1 1.0	30 min., 320°F	57.5	40	1300	250
36-D	Viton A 100 Lead Oxide 15 HBB 150 Diak #1 1.0	30 min., 320°F	73.5	100	370	50
35-C	Hypalon 40 100 Lead Oxide 15 M.B.T.S. 1.0	30 min., 310°F	29.9	20	2000	600
35-D	Hypalon 40 100 Lead Oxide 15 HBB 150 M.B.T.S. 1.0	30 min., 310°F	61.5	70	930	450
35A	Neoprene W 100 Lead Oxide 15 NA-22 1.0	10 min., 310°F	35.0	23	1950	400
35-B	Neoprene W 100 Lead Oxide 15 HBB 150 NA-22 1.0	10 min., 310°F	63.5	65	800	250
36-A	Hydrin 100 100 Lead Oxide 15 Diak #1 1.0	30 min., 300°F	33.6	20	980	600
36-B	Hydrin 100 100 Lead Oxide 15 HBB 150 Diak #1 1.0	30 min., 300°F	63.0	50	300	400

Note: HBB - Hexabromobenzene; M.B.T.S. - 2-mercaptobenzothiazole; Diak - Amine accelerator;
NA-22 - Accelerator

TABLE IV-2

VITON FORMULATIONS

Book #	Formulations (Parts by Weight)	Curing Condition (in oven)	% Halogen in Formulation	Oxygen Index	Tensile Strength (psi)	Elongation (%)
37-A	Viton A 100 Lead Oxide 15 HBB 150 TBCP 5 Diak #1 1	30 min., 320°F	74	75	500	200
37-B	Viton A 100 Lead Oxide 15 HBB 150 TBCP 30 Diak #1 1	30 min., 320°F	72.5	80	550	525
37-C	Viton A 100 Lead Oxide 15 HBB 200 TBCP 30 Diak #1 1	30 min., 320°F	74.5	85	420	500
38-A	37-C (See above) 90 XM-60 Prepolymer 10	30 min., 320°F	68.0	60	500	550
40-A	Viton A 100 Lead Oxide 15 HBB 200 TBP 30 Diak #1 1	30 min., 320°F	75.5	95	550	500
40-B	40-A (See above) 90 XM-60 Prepolymer 10	30 min., 320°F	69.0	60-65	600	500
41-A	40-A (See above) 80 XM-60 Prepolymer 20	30 min., 320°F	62.5	50	700	450

Note: HBB - Hexabromobenzene; TBCP - tris (bromochloropropyl phosphate)
TBP - tris (bromopropyl phosphate)

TABLE IV-3

CURING OF SYSTEMS FOR VITON

Book #	Formulations (Parts by Weight)		Curing Condition (in oven)	% Halogen in Formulation	Oxygen Index	Tensile Strength (psi)	Elongation (%)
39-A	Viton A	100	30 min., 320°F	73	75	720	450
	Magnesium Oxide	15					
	HBB	150					
	TBCP	20					
	Diak #1	1					
39-B	Viton A	100	30 min., 320°F	73	80	400	500
	Lead Oxide	15					
	HBB	150					
	TBCP	20					
	Diak #3	2.5					

Note: HBB - Hexabromobenzene; TBCP - tris (bromochloropropyl phosphate)

Since Viton formulations gave the best flame resistance of any material at lower loadings of flame retardant and the solvents were suitable for wet spinning, these formulations were selected for further evaluation. They were wet spun, cast into sheets and cut into thread. They were also melt spun.

In our early work we used the following standard formulation:

Material	Parts by Weight
Viton	100
Hexabromobenzene	200
Tris (2,3-dibromopropyl) phosphate	30
Hexanediamine Carbamate	2
Lead Oxide	15

With this formulation as a starting point, we evaluated various wet- and dry-forming methods of making thread. These techniques are discussed in detail in Section IV-B. With all of the methods, however, we had to make numerous changes in the materials and the die to form strong fibers.

2. Curing-System Changes

a. Evaluation of the Solvent

A wet-spinning technique similar to that for urethane was used to form fibers:

(1) The Viton formulation was mill-mixed with the flame retardants and curing ingredients, and dissolved in DMF (dimethyl formamide), MEK (methyl ethyl ketone), or acetone.

(2) The dissolved formulation (spinning dope) was pumped through a 40-hole spinnerette into a 180°F water bath.

(3) From the bath, the fiber was passed onto a Teflon belt and through a drying and curing oven.

Only the DMF solution resulted in the production of cohesive fibers and even these fibers were weak because they contained a high proportion of solvent that was difficult to eliminate and made the fibers difficult to handle.

Prior work with the Viton formulations in this program had always involved the use of dimethyl formamide (DMF) as a solvent for casting sheets. The curing behavior of the compounded stock in the absence of DMF had never been evaluated. Therefore, we mixed the standard Viton formulation on a two-roll mill and press-cured it for 30 minutes at 335°F.

Only a minimum cure was obtained and the product remained weak and highly extensible--characteristic of undercure. In contrast, Viton sheets of the same formulation cast from DMF solution exhibited about 90% of their ultimate physical properties when they were cured in a similar manner. (The remaining 10% was obtained after the sheets were post cured in an oven for 24 hours at ~ 400°F.) (See Section C for explanation)

b. Evaluation of the Cross-Linking Agents

In the curing system for Viton, metallic oxides cause hydrogen fluoride to be eliminated and leave unsaturated linkages that provide sites for cross-linking. The cross-linking agent typically is a difunctional amine.

We have evaluated two oxides (lead and magnesium), and two difunctional amines--Diak #1 (hexamethylene diamine carbamate) and Diak #3 (n, N-dicinnamylidene-1, 6-hexane diamine). Our conclusions are that:

(1) Magnesium oxide curing systems give higher strength but lower oxygen index values than lead oxide systems.

(2) Diak #1 gives better physical properties but lower oxygen index values than Diak #3 (70 versus 80). Furthermore, Diak #3, which melts at the extrusion temperature, facilitates extrusion of the fiber.

On the basis of our findings, we selected lead oxide in preference to magnesium oxide and replaced Diak #1 with Diak #3 in our formulation.

c. Plasticizer Changes

The T-23P used in the standard formulation serves three purposes. First, it is an excellent flame-retardant plasticizer. Second, it provides the necessary elongation. Third, it facilitates the extrusion of fibers. However, an evaluation of Viton sheets cast from solvents other than DMF and a study of formulations in which each ingredient was systematically eliminated from the standard formulation indicated that the T-23P was interfering with the cure. Apparently, when T-23P is heated to the cure temperature, 335°F, it partially decomposes and releases acidic fractions. Since the Viton cure requires basic conditions, in solvents much as acetone or MEK, the rubber did not cure. DMF, however, is itself somewhat basic, and probably neutralizes any acidic fractions that might be formed. Thus, the rubber could cure in this solvent. Nevertheless, because of the problems encountered with solvents other than DMF, we evaluated possible replacements for T-23P. Tricresyl phosphate (TCP) was found to produce Viton sheets that could be cured without difficulty.

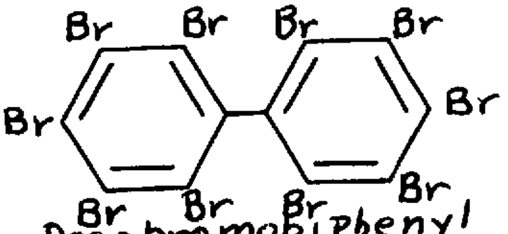
d. Flame Retardant

When the effects of varying the time and temperature of the cure cycle were examined, it was noticed that a much stronger and more elastic fiber resulted from a cure of 400°F for 16 hours. (See Figures IV-1, -2 and -3.) However, this fiber had lost a substantial portion of the flame-retarding filler, hexabromobenzene.

Although the hexabromobenzene is satisfactory in urethanes, where a high cure is not involved, it is too volatile at the cure temperature of the Viton. Consequently, other retarding agents were reviewed for use as a replacement.

Figure IV-1 shows the weight loss of the hexabromobenzene that occurs during cure. In six hours at 400°F it completely volatilizes from the stock. This rate will vary, of course, depending on air circulation in the oven and the thickness of the fiber. Figures IV-2 and IV-3 show the corresponding changes that take place in tensile strength and oxygen index with this weight loss.

In the early experiments in this program, many flame-retarding compounds had been screened for their effectiveness and compatibility with urethane and fluorinated elastomers. One of the best was decabromobiphenyl:



Decabromobiphenyl

Decabromobiphenyl has about the same bromine content as hexabromobenzene but is more thermally stable:

Material	% Bromine	Melt Temp.
Hexabromobenzene	87	306°C
Decabromobiphenyl	85	375°C

Since we believe that the DBBP would be better retained in the elastomer both during the cure and during pyrolysis of the fiber, the following fiber formulations were prepared and extruded into fibers:

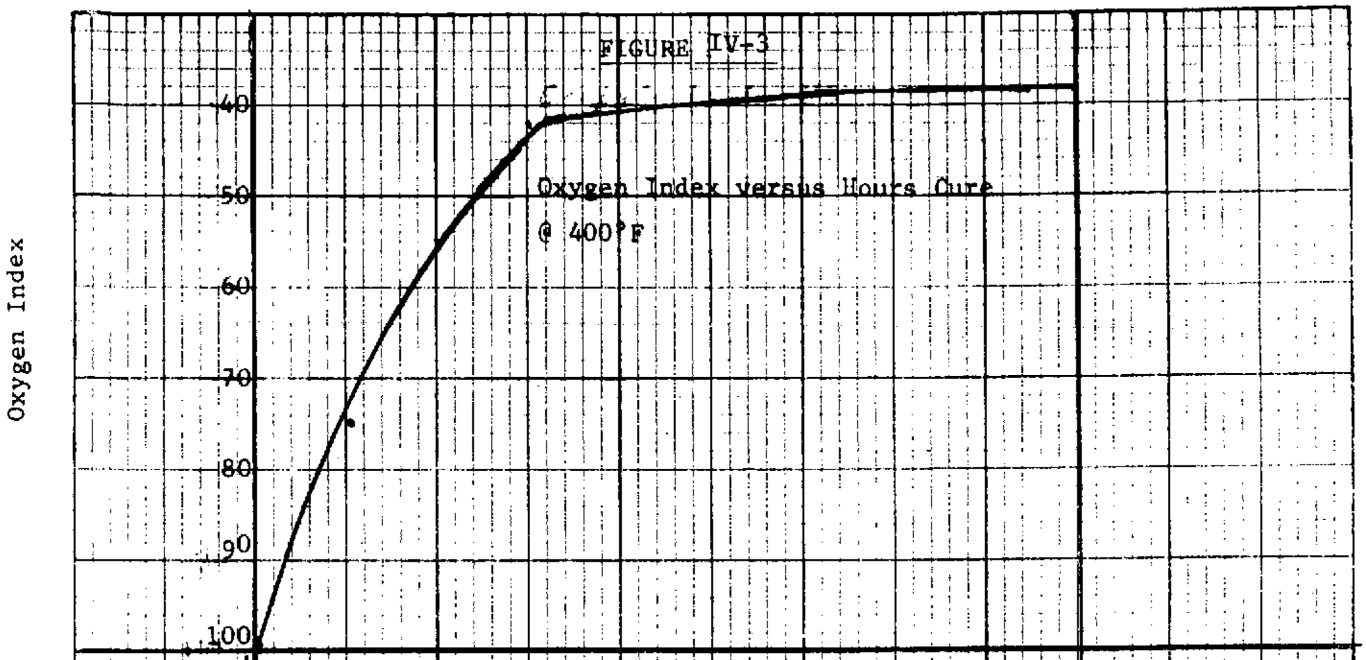


FIGURE IV-3

Oxygen Index versus Hours Cure @ 400°F

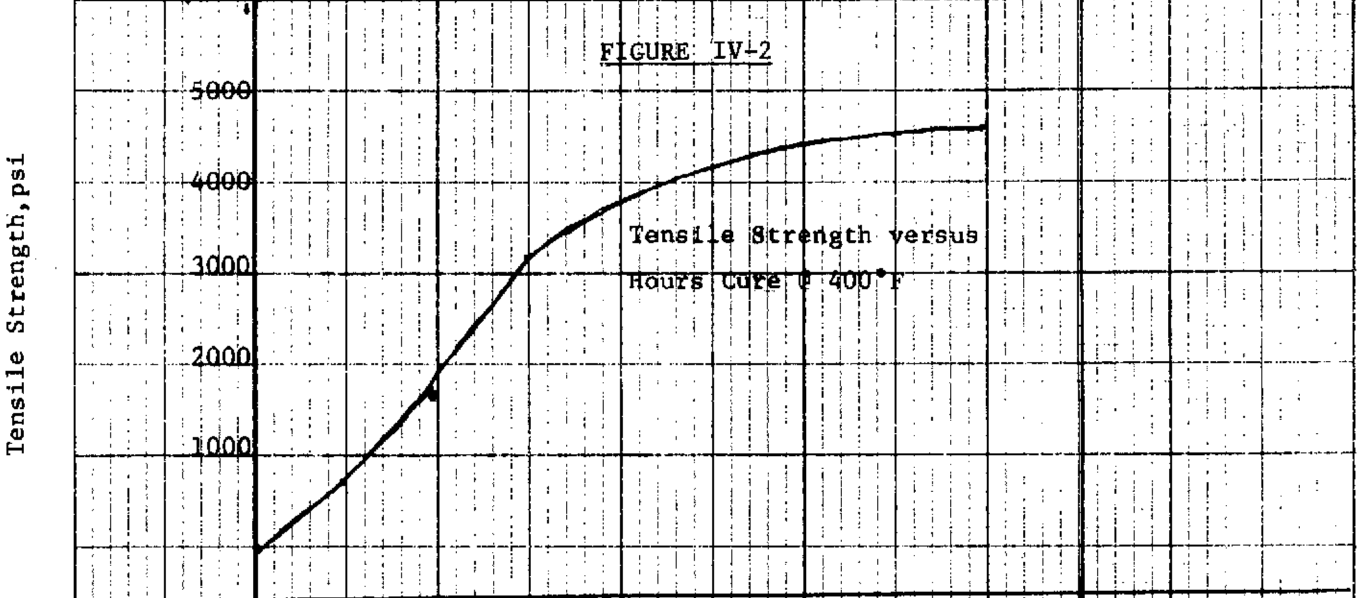


FIGURE IV-2

Tensile Strength versus Hours Cure @ 400°F

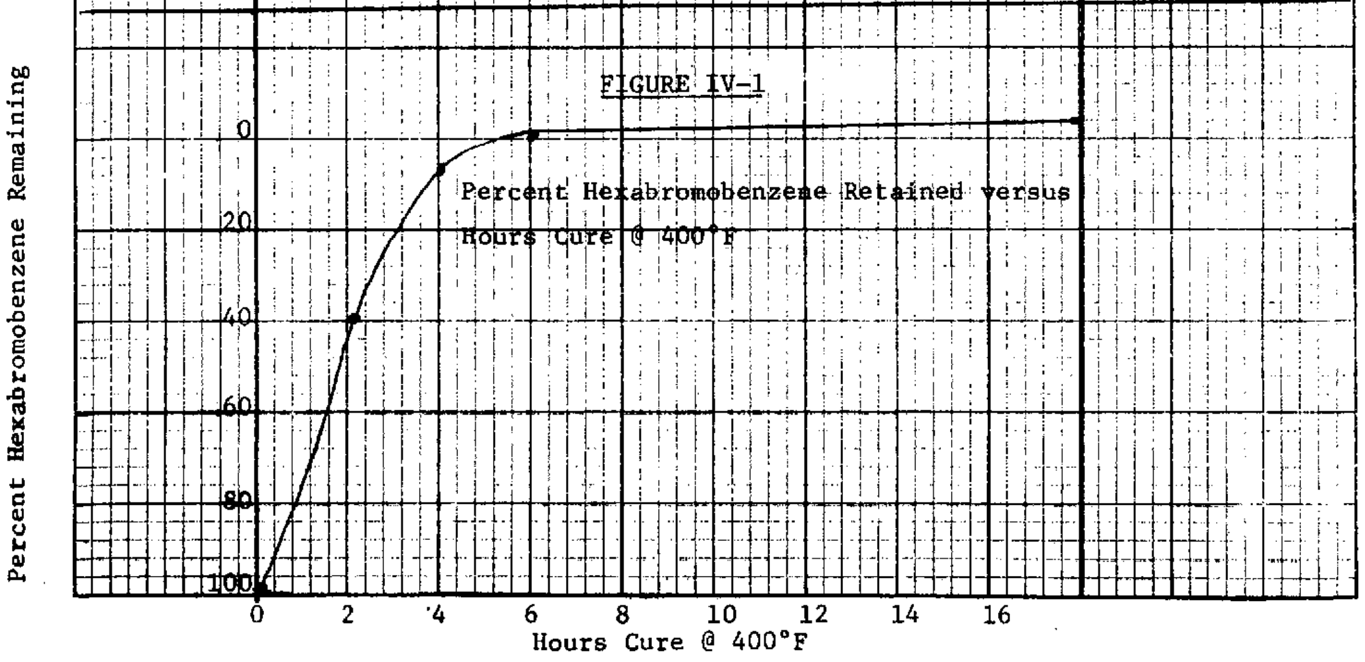


FIGURE IV-1

Percent Hexabromobenzene Retained versus Hours Cure @ 400°F

	1(DBBP)	2(HBB)	3(HBB)
Viton B	100	100	100
Decabromobiphenyl	100		
Hexabromobenzene		100	200
PbO	15	15	15
Tricresyl phosphate	10	10	10
Diak #3	4	4	4

When cured, the fibers exhibited the following properties:

	1(DBBP)	2(HBB)*	3(HBB)*
Tensile strength, psi	1300-1500	1500	700
Elongation, %	500-600	450	500
Oxygen Index	85	80	100

* Data derived from Figures IV-1, -2, and -3 because of weight.

During a 16-hour cure at 400°F, no measurable amount of the decabromobiphenyl was lost from the compound. Cure is complete in two hours, thereafter, the physical properties are under no further change. Oxygen index also remains constant. Thus, the decabromobiphenyl proved to be a satisfactory solution to the volatility problem.

This change of flame retardant, from hexabromobenzene to decabromobiphenyl, necessitated a review of the other ingredients in the formulation to be certain that the optimum physical properties were being obtained.

e. Other Compound Changes

In a related change, Viton A was replaced by Viton B to improve the elongation characteristics of the elastomeric fiber. This change allowed two-thirds reduction in the amount of plasticizer and, consequently, a higher tensile strength.

The formulations listed in Table IV-4 were extruded into fibers, cured at 400°F for 16 hours, and their physical and fire-retardant properties evaluated (Table IV-5).

TABLE IV-4

VITON FORMULATIONS EVALUATED

Ingredients	Control	65-A	65-B	65-C	65-D	65-E	65-F
Viton A	-	100	-	-	-	-	-
Viton B	100	-	80	80	100	100	100
Viton LM	-	-	20	20	-	-	-
Decabromobiphenyl	100	100	100	100	100	100	100

TABLE IV-4 (Continued)

VITON FORMULATIONS EVALUATED

Ingredients	Control	65-A	65-B	65-C	65-D	65-E	65-F
Zinc Oxide	-	-	-	-	-	10	-
Lead Oxide	15	15	15	15	15	-	15
Dyphos (dibasic lead phosphate)	-	-	-	-	-	10	-
Tricresylphosphate	10	10	10	-	-	10	10
Antimony Oxychloride	-	-	-	-	-	-	20
Diak #3	4	4	4	4	-	4	4
Diak #4	-	-	-	-	4	-	-

TABLE IV-5

PHYSICAL AND FIRE-RETARDANT PROPERTIES OF FIBERS

Fiber Formulation	Weight Loss on Cure (%)	Tensile Strength (psi)	Elongation (%)	Oxygen Index
Control	1.9	1500	450	85
65-A	6.9	1200	410	85
65-B	6.3	1200	450	85
65-C	5.0	1180	375	85
65-D	2.7	1400	250	85
65-E	7.3	1490	400	85
65-F	6.4	1240	350	85

B. METHODS OF MANUFACTURE

We evaluated four methods of forming fibers: wet spinning, cut thread, dry spinning and extrusion.

1. Wet Fiber Spinning

The technique and equipment used to spin the fluorinated rubber into fibers were the same as those used to spin urethane fibers. The compound was mixed on a rubber mill, ground into pellets and dissolved in dimethyl formamide. It was then pumped through the spinnerette into a water bath where it coagulated into fibers. The fibers were drawn from the bath into a drying oven, and dropped into a tray containing talc, which prevented the fibers from sticking together. The tray was then placed in an oven and cured for 24 hours at 400°F.

This process was extremely difficult to handle because the fibers--prior to their exit from the oven--contained residual solvent, were not completely cured, and thus were very weak. The process was discarded when extrusion methods proved more feasible.

2. Cut Thread

As an alternative to the above, we also cast the solutions (by reverse-roll coating) onto release paper as sheets 10 mils thick. The sheets were then cured and cut into thread. However, the thick sheets present drying and handling problems and a dry technique is preferred.

3. Dry Spinning

Dry spinning was considered as a possible fiber-forming method because high-temperature air could be impinged on the fibers as soon as they emerged from the spinnerettes. The air would serve to both remove solvent and initiate the curing reactions.

To evaluate this approach, we set up a pipe chimney through which hot air (~150°C) was fed. A monofilament fiber was then spun from a syringe into the top of the pipe.

The results of these experiments were disappointing because the fiber, instead of coagulating and curing, tended to neck down and break. As a result, a continuous length of spun fiber could not be wound on the take-up reel.

4. Extrusion

Extrusion of the fibers proved to be the least troublesome method of making fibers and it was the technique to which we devoted a major portion of our time. The basic process is described below along with the various improvements incorporated as our work progressed.

Except for the decabromobiphenyl, we used ingredients as received from the suppliers. The decabromobiphenyl was purified by recrystallization from trichlorobenzene and then ground in an air mill to reduce the particle size to about 1μ.

The ingredients were blended on an unheated two-roll mill. Each formulation was then granulated to particles about 1/16" in diameter and fed to the extruder (Figure IV-4) where it was converted into 12 continuous filaments having diameters of about 13 mils. The extruder was run at 50% of capacity, producing approximately one-third of a pound of fiber per hour--(equivalent to 2000 ft/hr of fiber). As the fibers exited the die (Figure IV-5), they were directed individually through guides (Figure IV-6) to vessels where they were collected in coiled form.

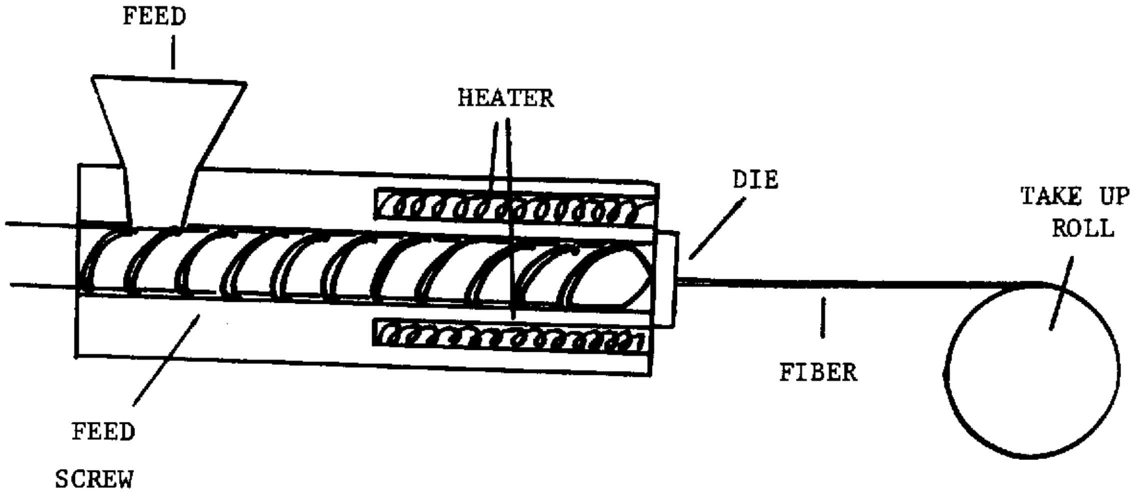


FIGURE IV-4

FIBER EXTRUDER

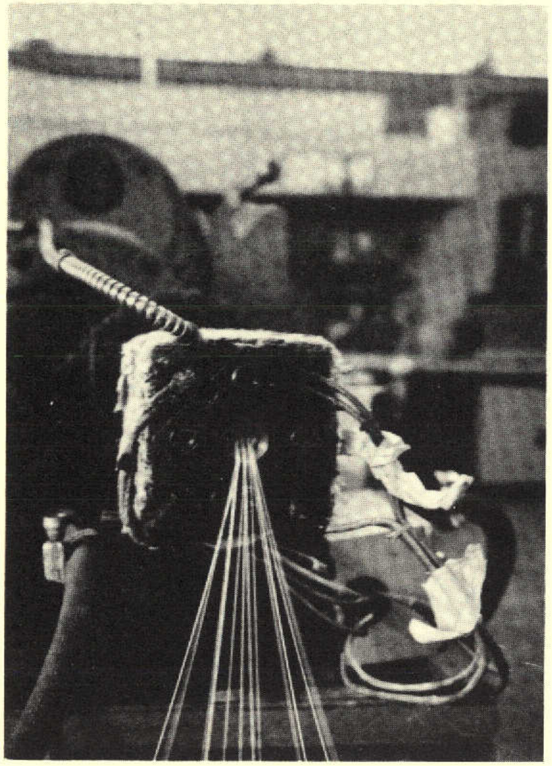


FIGURE IV-5

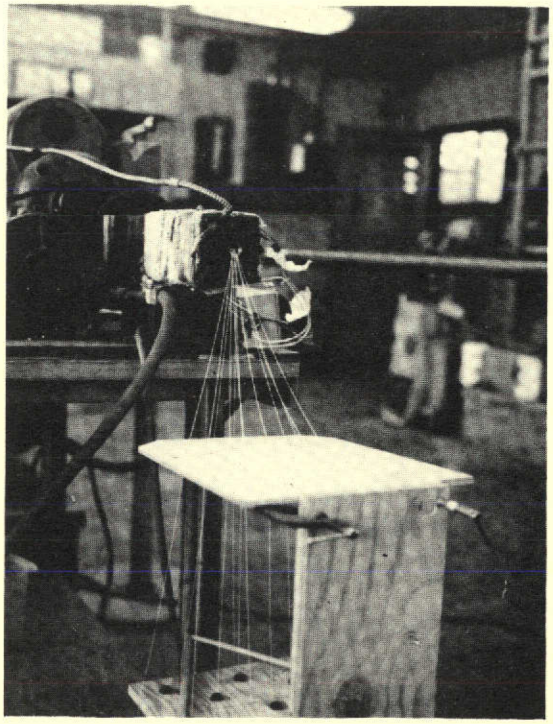
TWELVE FIBERS

EXITING EXTRUDER DIE

FIGURE IV-6

FIBERS FEED THROUGH GUIDES

TO COLLECTING VESSELS



The fibers were removed from the vessels and uncoiled in pyrex trays into an open, loose pattern. During the uncoiling procedure, the fibers were sprinkled liberally with talc to prevent fiber-to-fiber adhesion.

The trays were then placed in air-circulating ovens at 400°F for 16 hours. After this cure, the fibers were wound on spools--ready to be knit or woven.

a. Release Agents

One of the major problems encountered in the early trial runs was the tendency of the uncured fibers to stick together as they came out of the extruder and were rolled up. Separating the fiber and placing it in trays, therefore, was largely a hand operation. Consequently, various release agents were evaluated for their ability to prevent fiber-to-fiber adhesion during the wind-up and cure (Table IV-6).

Talcum proved to be the most suitable. The Freon preparations, although good release agents, weakened the fibers either by penetrating into the fiber and causing it to swell, or by leaching out some of the tricresyl phosphate. The net result is that the fiber tends to break under the tension of the take-up.

This problem can be alleviated somewhat by using a lower boiling Freon mixture that will flash off before significant penetration occurs. For example, Freon TF, with a boiling point of about 118°F, can be mixed with Freon 11 to give a solution that boils at 70-80°F. However, we did not pursue this approach because the talcing procedures provided adequate release and because Freon vapor represents a breathing hazard.

The application of talc to the fiber has been automated through the use of a mechanical shaker so talc is continuously applied to the fibers as they exit from the die face. An initial concern with the hazard talc dust has been dealt with by building an enclosure around the shaker and take-up rack. An exhaust blower ensures that the enclosure is always under a negative pressure.

b. Powered Fiber Take-off

A powered fiber take-off rack was built to carry the fibers horizontally away from the die face. The advantages of the new rack over the previous vertical arrangements include better access to individual fibers, uniformity of fiber take-off speed, provision for 20-30 fibers, and amenability to set-ups where release agents can be applied continuously to the entire fiber surface area.

TABLE IV-6

EFFECTIVENESS OF RELEASE AGENTS

AGENT	COMMENTS
Silicone emulsion, SM-2040 (G.E.)	
1%	fair release-weak fiber
35%	fair release-weak fiber
Silicone emulsion, LE 420 (Union Carbide)	
1%	fair release-weak fiber
35%	fair release-weak fiber
Silicone oil, Dow 710	fair release
Dow 200, 50CS	poor release
Aquarex L, (duPont), 5% in water	poor release-weak fiber
Aquarex WAQ, (duPont), 5% in water	poor release-weak fiber
Talcum, U.S.P.	good release-strong fiber
Talcum, U.S.P. water slurry	poor release-weak fiber
Silica, Silanox (Cabot Corp)	good release-weak fiber
Bentonite slurry, 2% in water	poor release-weak fiber
2% in water and 1/2% Alkanol HCS	poor release-weak fiber
Teflon in water (1-5μ particle size)	med. release-weak fiber
1. Teflon in Freon TF (1-5μ particle size)	med. release
Fluorocarbon telomer dispersion in water	med. release-weak fiber
Fluorocarbon aerosol spray (M/S)	good release-fair fiber
Fatty acid soap solution	poor release-weak fiber
Calcium stearate slurry in water	poor release

1. Vydax AR

c. Die Design

The production of stretch fabric from elastomeric fibers requires a high degree of uniformity of both fiber dimensions and fiber physical properties. Since the elastomer is incorporated into the fabric construction in an elongated configuration, any variation in retractile power will be reflected in a puckering and distortion of the fabric.

In initial fiber-producing trials various factors were evaluated including die designs; die shrinkage characteristics, ability to draw fibers down, and optimum number and size of die holes. A die containing twelve 0.013-inch-diameter holes was finally selected because it had a good combination of easy extrusion, high throughput and small fiber diameter.

Fibers cured in a forced convection oven for 16 hours at 350°F showed the following properties:

Tensile Strength	700 psi
Elongation	250%
Oxygen index	100
Oxygen index*	65

Variations in die design were evaluated to ensure that the multiple fibers exiting the die have equivalent diameters. Die holes with an entrance angle of 20° and a length/diameter ratio of 8/1 have proven successful (Figure IV-7). The geometrical pattern of the holes also has been examined to establish a design that will facilitate fiber take-off from the die face (Figure IV-8).

DIE-HOLE DESIGN DIMENSIONS

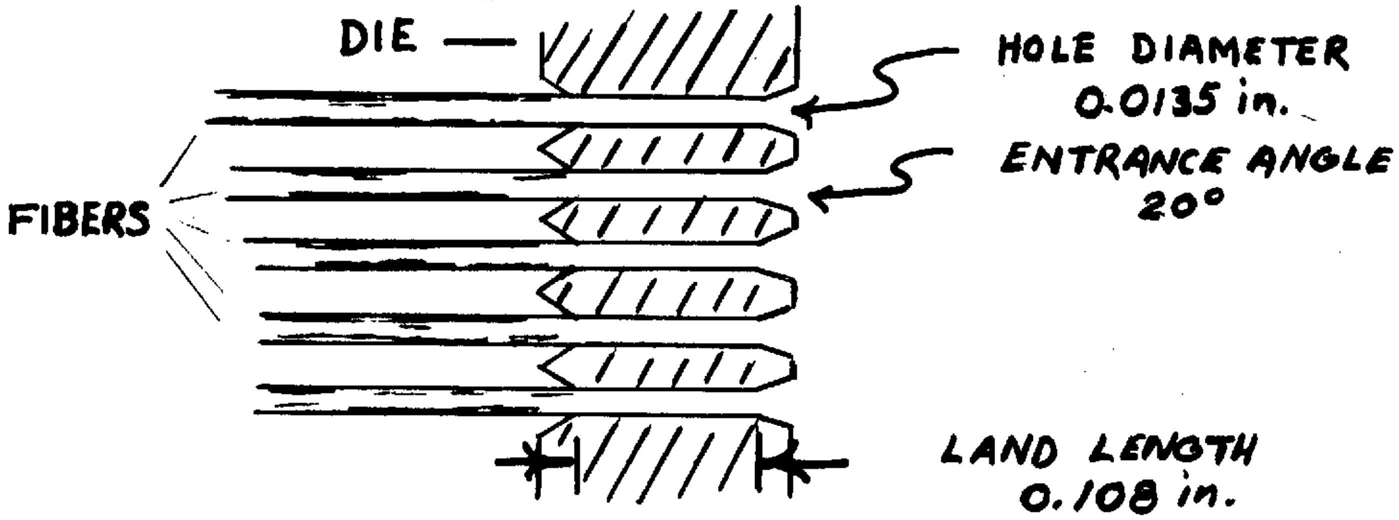


FIGURE IV-7

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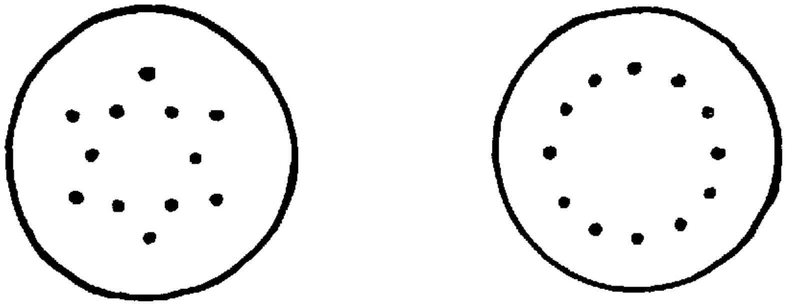
* Under continuous hydrogen flame source

FIGURE IV-8

Figure IV-8A is the preferred design

Figures A and B illustrate two of the twelve-hole designs that have been prepared.

TWO 12-HOLE PATTERNS



A. B.

The die, with a land-length to hole diameter of 8:1 and an entrance angle of 20°, was evaluated at extrusion rates of one-third and two-thirds of a pound per hour. The results are in Table IV-7.

TABLE IV-7

EFFECT OF EXTRUSION RATE ON SIZE AND UNIFORMITY OF FIBER DIAMETER EXTRUDED FROM 12-HOLE HEXAGONAL PATTERNED DIE

	Fiber Diameter	
Fiber	at 1/3 lb/hr	at 2/3 lb/hr
1	12 mil	13 mil
2	12.5	13
3	12	12.5+
4	12.5	13
5	12	13
6	12	13
7	12+	13
8	12	12.5
9	12	13
10	12	13
11	12.5	13
12	12.5	13+

At a constant extrusion rate the fiber diameter varies by less than 5%. This uniformity is to be expected; the pressure of the material being extruded against the die face should be essentially constant (independent of radial position), because the pressure drop through the die is much greater than the pressure drop parallel to the die face. With a scres extruder, though, there is always the possibility of cyclic pressure pulsations in front of the lead flight of the screw. However, no significant variation in diameter was found along the length of individual fibers.

C. FABRIC PREPARATION

1. Circular Knitting

The simplest and most common methods of introducing elastic fiber into a circular knit structure are: knitting-in, laying-in, wrapping, and plating. The techniques of knitting-in or laying-in the elastomeric yarns can be employed on both jersey (single-needle cylinder) and rib (cylinder and dial) machines. In general, however, it is preferable to knit-in rather than lay-in the elastic, because the former produces a construction with two-way stretch.

In laying-in, the elastomeric fiber typically appears as straight weft threads within the knitted structure. In this case, stretch is exhibited only in the weft direction. In knitting in, on the other hand, the elastomeric fiber is alternated with the nonelastic fiber in the construction of the knitted structure. In this case, stretch is exhibited in both weft and warp directions.

Wrapping has much to recommend it as a procedure for incorporating elastic fiber into a fabric. The elastomer is introduced in the weft direction on a jersey basis, and nonelastic wrapping yarns are introduced in the warp direction. If the wrapping yarn is made moderately elastic, for example, by a texturizing process, a resilient fabric possessing lengthwise stretch will result. If, in addition, a highly elastic flame-retardant fiber, such as Viton, is fed on a knit-in basis in the warp direction, a two-way stretch fabric will be produced.

Plating involves the simultaneous feeding of two yarns, one to appear in the face of the fabric and the other on the reverse. This construction does not exhibit as great a stretch as do the others, but plating can be used to produce a rubberized liner for good adhesion or sealing, for example.

2. Warp Knitting

The so-called "power net" fabrics, exhibiting excellent two-way stretch characteristics, are typically produced by warp-knitting techniques. Two warps are used--an elastic one and a nonelastic one. The elastic warp may be prepared with either bare or covered flame-retarded Viton. Choice depends on the fabric construction and the power desired. The use of bare Viton makes for lighter and more supple fabrics because there are not covering yarns to add to the weight of the structure. On the other hand, by using covered Viton, the amount of fabric stretch can be controlled to take full advantage of the elastic fiber's modulus characteristics. The elastomeric fiber may be covered with Beta Fiberglas, PBI, Durette or other othermally stable nonelastic fiber to produce flame-resistant stretch fabric with excellent power.

At the time work on this phase was carried out there was only a limited amount of PBI multifilament available of less than 100 filaments (the equivalent of 200 denier) and 200 denier monofilament. Nomex could only be treated in the fabric form so that it would pass the 70% oxygen/30% nitrogen flammability test and treatment conditions were too severe for the rubber component if it was incorporated prior to treatment. For these reasons, the major part of the work was with fiberglass for the purpose of evaluating stretch and recovery characteristics of different structures.

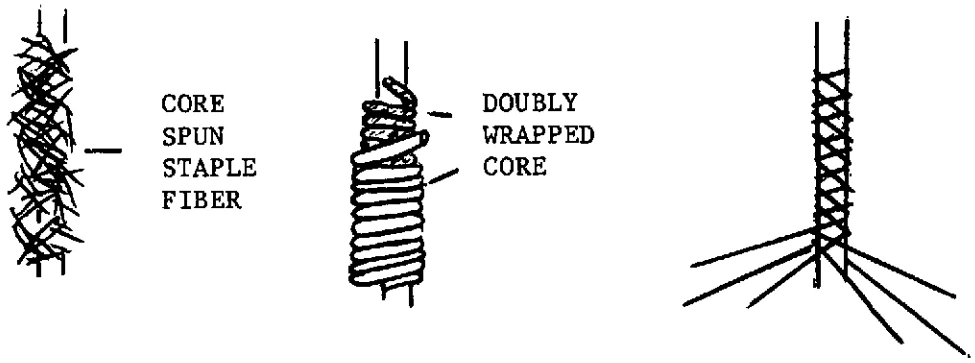
3. Knitting Experiments

Our first step in developing a fabric structure was to evaluate different methods of covering the fiber. At the beginning, we started with our urethane fibers, which were relatively weak, because we had not yet determined the best fiber formulations or processing techniques. Fibers were not uniform and had low tensile strengths.

The wrapping techniques considered were core spun staple fiber, double wrapped core, and core twisting or braiding (Figure IV-9).

FIGURE IV-9

ELASTOMERIC FIBER, TYPES OF WRAP



CORE SPUN   CORE WRAPPED   CORE TWISTED

a. Urethane Fibers Braided With Fiberglass

A 180-210 denier flame-retardant spandex was sent to F.W.F. Industries to be covered with a braid of 450/1-0 Beta Fiberglas. The elastic fiber proved to be difficult to cover because Beta Fiberglas fibers (3.5 microns diameter) could not be drawn tight enough in the braid to cinch the 180-210 denier elastic fiber in the core. When the same braiding technique was applied to 210 denier Lycra fiber (duPont), an elastic yarn was easily produced. The difficulty with the flame-retardant spandex stemmed from its finer diameter and irregular cross section. Methods of overcoming the problem would be to increase the diameter of the elastic core or decrease the diameter of the covering fibers. The diameter of the elastic core can be increased easily by using two or three spandex fibers in the core instead of one. The diameter of the covering fiber can be reduced if fine-diameter X-420 or PBI is used in place of the 450/1-0 Fiberglas.

As discussed previously, the flame-retardant urethane formulations have inherently lower strength at any given level of flame retardancy than the modified Viton. For this reason, all further wrapping and knitting experiments were carried out with our modified Viton fibers.

b. Modified Fluorinated Rubber Fibers and Fabrics

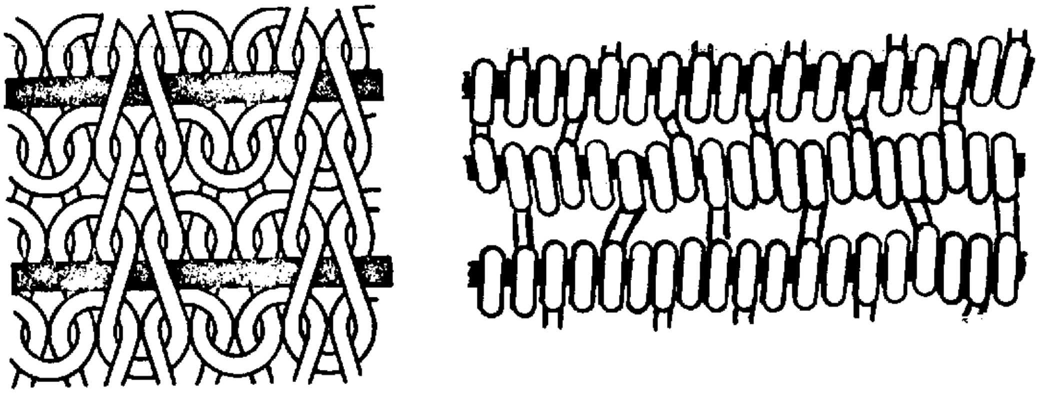
The initial samples of power net fabric prepared for evaluation were circular knits constructed from Viton fibers covered with a Beta Fiberglas braid. The easily fabricated circular knits could be produced with a minimum quantity of material and were suitable for initial screening evaluations, but they were not representative of the fabrics that would ultimately be produced by flat-bed knitting techniques.

The standard commercial power net fabrics are usually made on Raschel knitting machines using a two-warp system--one elastic, the other nonelastic. The power net material selected by NASA as the model to be duplicated with flame-resistant materials exhibited an elastic warp formed with bare spandex. To duplicate this construction, two warp beams--one of bare Viton fibers, the other of thermally stabilized PBI--have to be formed and knitted. Since this would require a substantial amount of fiber, the preliminary experiments were carried out on the circular knit.

Because the previous experimental work involved covered elastomer only, a question arose as to the flame resistance of constructions incorporating bare elastomer. Consequently, we prepared a circular knit of Fiberglas,on the back of which was laid bare Viton fiber (Figure IV-10B). This material was tested at NASA-MSC in the Silicone Igniter Test in an environment of 70% oxygen, 30% nitrogen and was found to be self-extinguishing. Since the Viton in the Raschel knit will be covered more completely by the nonelastic fibers than it was in the simulation, we do not anticipate any problems with the flame resistance of the Raschel knit power net fabric.

FIGURE IV-10

KNIT PATTERNS



A. Simulated Raschel Knit B. Raschel Knit

Prototype fabric samples were prepared to evalute the versatility, elastic power, and flame resistance of the flame-retardant Viton elastomeric fiber. The fiber was combined with Beta Fiberglas, Nomex, and PBI in warp knit, jersey rib knit, and other circular knit constructions. Machine settings were explored to elongate the fiber for optimum elastic power. Flame-resistant fabrics exhibiting good two-way stretch were prepared. These might be useful for sleep-restraint harnesses, liquid cooling garments, instrumented head caps, and other applications where a stretch fabric is needed.

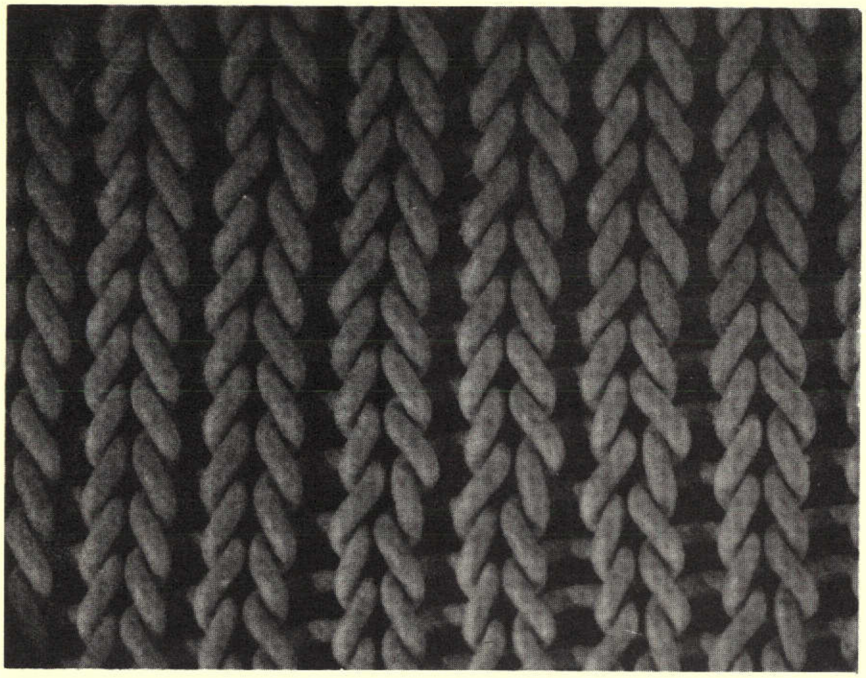
Figures IV-11A and B are jersey knits produced entirely from 800-denier flame-retardant Viton fiber. By varying the number of needles around the knitting cylinder, we were able to adjust the density of the knit. These fabrics have two-way stretch.

Figure IV-12A is a warp-knit, 36-gauge power net produced from 800-denier Viton and 200-denier continuous filament Nomex. This fabric has two-way stretch. Figure IV-12B is a warp knit similar to that shown in Figure IV-12A except that the machine was adjusted to give a "broad weave" pattern.

Figure IV-13 is a 120-needle jersey knit consisting of Beta Fiberglas 150's. Viton fiber, elongated 50-70%, has been laid-in in a weft direction. This fabric exhibits stretch in the weft direction only.

c. Power Net Fabric From Thermally Stabilized PBI

PBI fiber, which is normally not flame resistant in a 70% oxygen/30% nitrogen environment, has been made self-extinguishing in this atmosphere through a process developed by Fabric Research Laboratories, Inc. (FRL). Even after receiving this process, the fiber



A. 120 NEEDLES

B: 160 NEEDLES

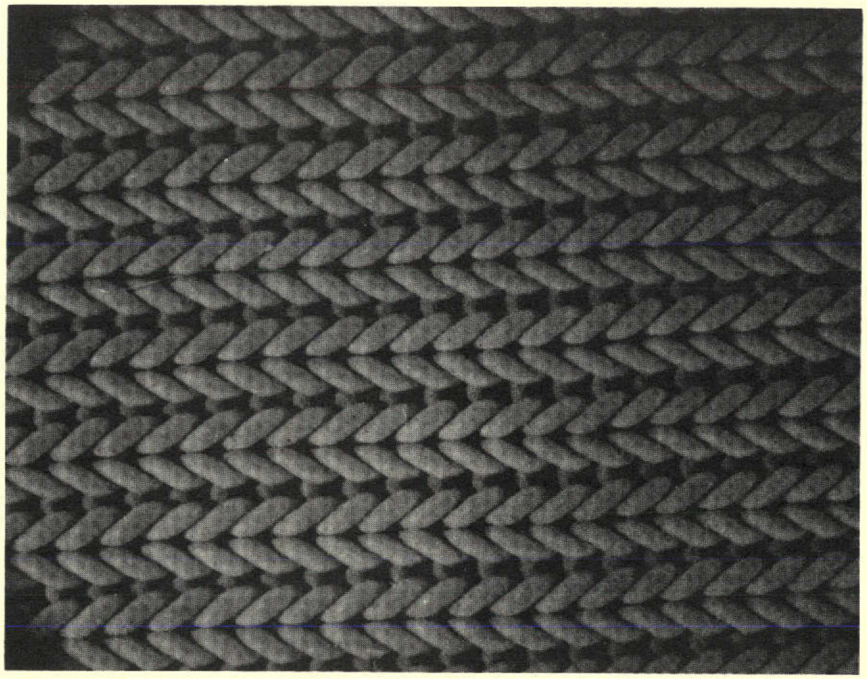


FIGURE IV-11

ELASTIC FIBER JERSEY KNIT

(Magnification 10K)

A: 800
DENIER ELASTIC
FIBER, 200 DENIER
CONTINUOUS FILAMENT
NOMEX

B: OPEN KNIT

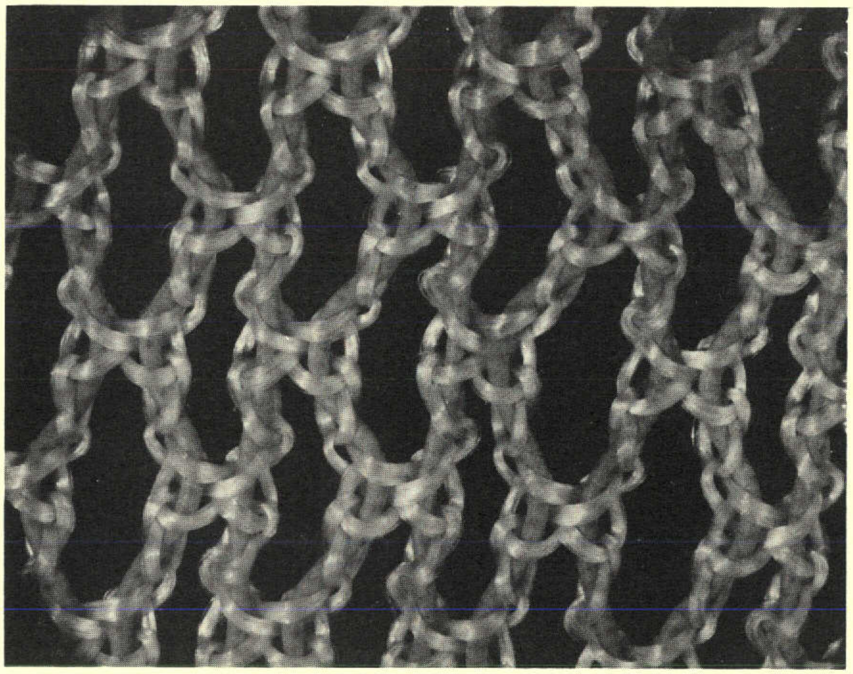


FIGURE IV-12

WARP KNIT POWER NET FABRIC

(Magnification 10K)

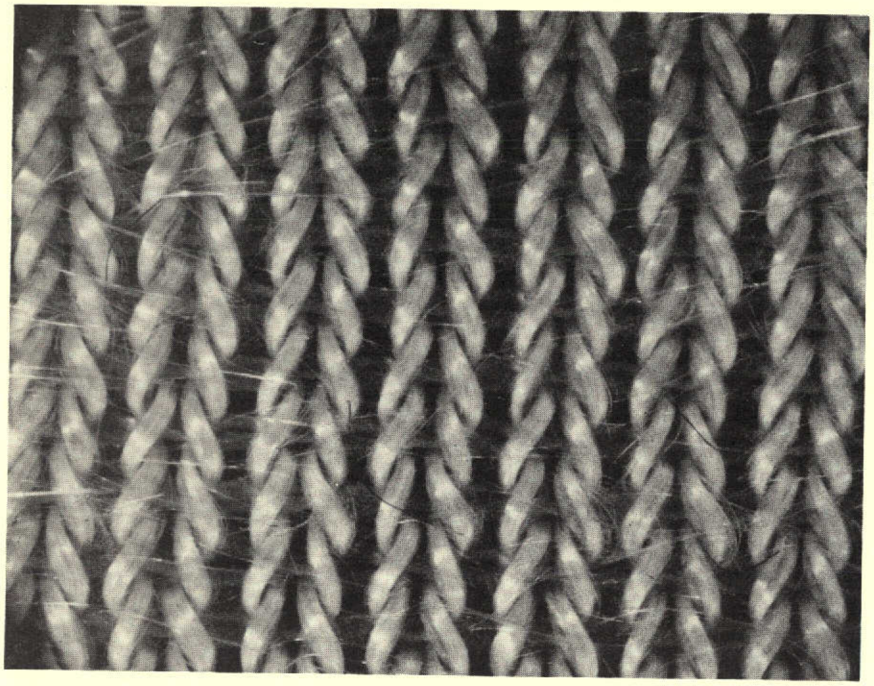


FIGURE IV-13

JERSEY KNIT BETA FIBERGLAS 150's WITH ELASTIC FIBER LAID IN

(Magnification 10K)

retains the desirable textile properties of hand, drape, and abrasion resistance that recommend its use as the nonelastic component in the power net fabric.

To determine if the FRL process could be applied to the PBI in the power net without adversely affecting the Viton fibers, we sent samples of Viton fiber (Control formulation) to FRL for exposure to their process. The results of this evaluation (Table IV-8) indicate the elastic fiber will not be affected. Urethane is, however.*

TABLE IV-8

EFFECT OF FRL PROCESS ON PROPERTIES OF VITON FIBER

Fiber	Tensile Strength (psi)	Elongation (%)	Oxygen Index
Control	1560	400-450	85
FRL #1901-16-1	1625	400-450	85
FRL #1901-16-2	1520	400-450	85

d. Fabric Properties

The flame-retardant Viton fiber does not have quite the strength of a spandex fiber of the same denier. However, the properties of the two fibers are sufficiently similar to permit essentially equivalent power net fabric structures to be prepared. A comparison of the tensile-elongation behavior for the two fiber types is given in Table IV-9.

Because of the lower tenacity of Viton fibers, it is necessary to use larger diameter fibers to achieve equivalent retractile power. Figure IV-14, for example, shows that a 13-mil-diameter Viton fiber and a 6-mil-diameter Lycra fiber have very similar load-elongation curves.

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* In later work at FRL, a process was developed to treat PBI yarn; therefore, it is not necessary to treat the finished fabric.

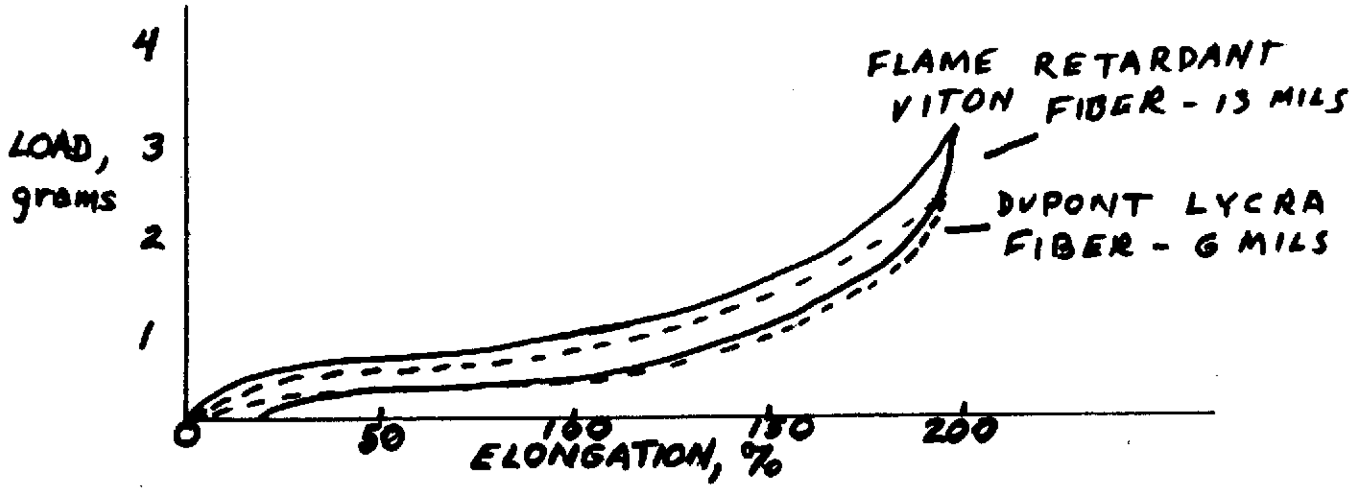


FIGURE IV-14

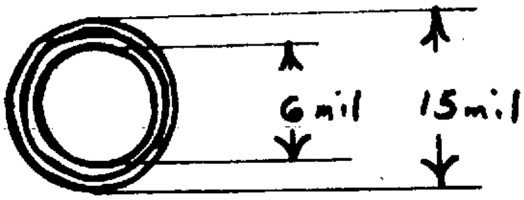
DIFFERENCES IN RETRACTILE POWER

TABLE IV-9

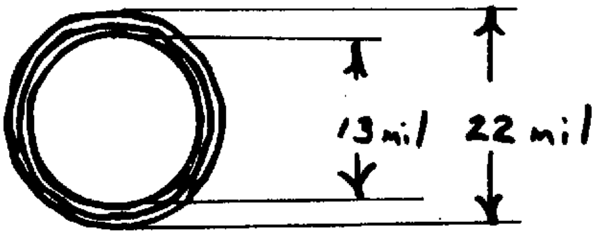
COMPARISON OF FIBER PROPERTIES

Property	Flame Retardant Viton	Lycra (duPont)
Elongation at Break	450%	500-600%
Power on second cycle at 50% elongation	100 psi	540 psi
Power on second cycle at 100% elongation	158 psi	900 psi
Power on second cycle at 200% elongation	485 psi	2700 psi

Consequently, Viton-based stretch fabrics that duplicate the properties of spandex constructions may be prepared by using Viton fibers that have double the diameter of their spandex counterparts. Since the fabric constructions usually employ elastomer wrapped within nonelastic fiber, the total diameter of the wrapped elastomeric fiber will not be doubled. In a typical construction employing 210-denier spandex and a double wrapping of 90-denier fiber, the total fiber diameter is about 15 mil:



In a Viton structure exhibiting equivalent power, a total double-wrapped fiber diameter of only 22 mils will be required:



A yarn of 50 singles or higher single wrapped will reduce fabric weight and will give optimum texture. Furthermore, the elastomeric fiber denier can be reduced if required. Thus, changes that may be made include deduction of PBI weight and reduction of elastomeric fiber diameter.

Although the fiber with 100 parts of decabromobiphenyl passes the specification when it is knit into a fabric, we have not determine/ the minimum level of decabromobiphenyl that can be used in a given fabric construction and pass the specification. As decabromobiphenyl level is reduced, strength increases. Thus, if lower levels can be used, and we believe this is possible, equivalent strength can be achieved at lower deniers