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Final Report

DEVELOPMENT OF A FLAMEPROOF ELASTIC ELASTOMERIC FIBER

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
MANNED SPACECRAFT CENTER
HOUSTON, TEXAS 77058

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FINAL REPORT

1 January 1970 to 1 January 1971

DEVELOPMENT OF A FLAMEPROOF ELASTIC ELASTOMERIC FIBER

by

J. T. Howarth, J. Milgrom, A. Massucco, and S. G. Sheth -- ADL
F. Dawn -- NASA

TO: National Aeronautics & Space Administration
Manned Spacecraft Center
Houston, Texas 77058

Contract: NAS 9-10424

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Arthur D. Little, Inc.

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ABSTRACT

To improve the flame resistance of elastic elastomeric fibers (Spandex urethanes) we have synthesized long-chain flexible urethanes that are more flame resistant than any that are commercially available, and we have also developed flexible urethane compounds by compounding urethanes with halogenated additives. These procedures have yielded products that are flame resistant even in environments containing 100% oxygen.

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 were 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 5,000 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 have been achieved depending on the levels of additives used. Compositions have been prepared and tested to meet the following specifications:

(a) 35% Oxygen/65% Nitrogen: These urethane compounds have tensile strengths of 1,500-2,000 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) 70% Oxygen/30% Nitrogen: These urethane compositions have tensile strength values of 400 to 900 psi, elongations of 250 to 400%, and oxygen index values of 75 to 85. They are composed of about 5% urethane, 20-30% fluorinated polymer, and 65-75% hexabromobenzene/trisbromochloropropyl phosphate.

(c) 100% Orlon: These compositions have tensile strengths of 400-700 psi and elongations of 250-400%. These materials contain about 2-1/2% urethane and 20-30% fluorinated rubber. The remainder is hexabromobenzene with 2-3% tris-bromochloropropyl phosphate to act as a plasticizer.

Fibers were made from the compositions we prepared. The procedure consisted of pumping the spinning dope through a spinneret with 40 ends, dropping the fibers into a water bath where they were precipitated, and running them through nip rolls and a dryer. Our prototype equipment simulated standard production procedures.

The composition of the elastic elastomeric fibers must be refined to give the fibers maximum strength and flame retardancy. Micrographs of these fibers show a somewhat porous structure, which accounts for their low strength. The structure will have to be improved, probably by modifying both the composition of the spinning solution and the spinning equipment.

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I. INTRODUCTION

In space exploration, extravehicular activity (EVA) is essential. Such activity requires high-strength elastomeric materials to fabricate both garments and carrying bags used in EVA.

The elastomeric fibers must have good strength, elongation, modulus, and recovery over the temperature and pressure ranges encountered in the space equipment. Because of the high oxygen atmosphere in the space vehicle, they also must be flame retardant. The polyurethanes (Spandex) are one of the few materials that have the required mechanical properties and the recovery characteristics, but they are not flame retardant. The purpose of this project was to develop techniques for imparting the necessary flame retardant properties to the flexible urethane structure so it would be suitable as a fiber in space exploration activities.

To attain this objective we synthesized urethane polymers with halogens on the polymer backbone and combined these with organic halogen-containing additives. We have prepared both films and fibers that meet the flame retardancy requirements, but the physical properties of the compositions need to be improved and formulated with halogen-containing additives.

II. BACKGROUND

A. ELASTOMERS

In view of the requirements for the elastic elastomeric fiber (which were based on the properties of duPont's Lycra), we first used polyurethane alone and modified it in various ways with nonelastomeric additives. As the program progressed, however, it became obvious it would be helpful to properties if part of the flame retardant additive was elastomeric and if flexible fluorinated polymers were used as part of the system.

1. Polyurethanes

Polyurethanes can be either rigid or flexible. The flexible fibers have been given the generic term Spandex, and they are unique among polymers in their strength and recovery characteristics. The term Spandex includes elastomeric fibers in which at least 85% of the fiber-forming substance consists of segmented polyurethane.

The elastomeric polyurethanes used to make "Spandex" fibers may be modified via the synthesis route to produce elastomeric fibers with good physical properties and improved flame resistance. These polyurethanes are commonly called segmented, because they consist of an alternate arrangement of "soft" segments consisting of either polyester or polyether urethane blocks and "hard" segments that generally contain aromatic urea and sometimes urethane groups as the rigid components. These rigid components are derived from the reaction of isocyanates with urea-producing compounds such as amines, hydrazines, and water. Hydrazine is a superior amine for producing the rigid components, and in our investigation we used primarily hydrazine as the coupling agent. The typical diisocyanates used in elastomeric fiber synthesis are derived from diphenylmethane and toluene – MDI and TDI, respectively.

The reaction of diisocyanates with hydrazine yields a polyurethane

$$[-RNH\overset{\overset{\displaystyle O}{\|}}{C}NHNH\overset{\overset{\displaystyle O}{\|}}{C}NH-]_n$$

that results in tough films and fibers. Hydrazine hydrate also can be employed in this preparation because the reaction of the isocyanate with the amino group proceeds more rapidly than with water. Moreover, hydrazine reacts readily in solvents such as dimethylformamide. The polyurethane from hydrazine hydrate and MDI gives a fiber that decomposes at about 300°C.

The "soft" sections of the segmented polyurethane, which impart the ability to elongate, are long segments; commonly have a molecular weight of 800-3000, and normally melt below 50°C. The "hard" sections, which tie the elastic chains together by hydrogen bonding or crystallite formation and essentially behave as crosslinking points, are short segments and typically have very high melting points, as noted above for the reaction of hydrazines and MDI. Thus, the chemical composition of the Spandex fibers may vary greatly, depending upon the nature of the segments in the polymer. Efforts to impart flame resistance to these fibers involved primarily the chemical modification of the "soft" segments. It is here that we introduced halogen-containing moieties.

These polyurethane fibers are prepared by treating a hydroxy-terminated polyester or polyether diol with the diisocyanate, usually at temperatures between 80°C and 100°C, to give a syrup that is called the prepolymer. Normally about two moles of this isocyanate are used for each mole of the glycol to insure that the prepolymer molecules are terminated on both ends by an isocyanate group. It is important in these preparations that the diols be pure in terms of functionality – the presence of triols is particularly harmful. The reaction time in the preparation of the prepolymer is important since there is a tendency to form side branches (allophanates) during this reaction. The isocyanate-terminated prepolymer is then usually dissolved in anhydrous dimethylformamide and an aliphatic diamine or, preferably, hydrazine is added in amounts equivalent to the diisocyanate. For optimum results, the final urethane polymer should have an inherent viscosity of 1-4, as measured in dimethylformamide. The highly viscous solution containing the final polymer is then spun, employing techniques similar to those used for polyacrylonitrile or cellulose acetate fibers. For the preparation of filaments, generally very little gel formation or crosslinking can be tolerated.

As mentioned above, both polyester and polyether diols have been used in the synthesis of elastomeric fibers. The most useful polyether is polytetramethylene glycol. Because this ether is very linear and has a tendency to form crystallites, the polytetramethylene glycol with a molecular weight of about 1,000 is treated with TDI to yield a 2,000-molecular-weight, hydroxy-terminated prepolymer. The polyesters used in the production of Spandex fibers usually consist of a mixture of adipic esters of ethylene and propylene glycol with a molecular weight of about 2000. Normally the esters are terminated with ethylene glycol because glycols containing secondary hydroxyl groups yield polymers of low melting point and decreased thermal stability.

A few commercial polyether diols are available that contain bromine and phosphorus (Swift and Company; Mobil Chemical Company). These commercial products were used in our initial investigation.

2. Polyester Modifications

The polyesters are most easily modified because one can use a mixture of carboxylic acids and glycols in their preparation. Therefore, we concentrated most of our effort in preparing halogen-containing polyesters.

A variety of routes are available for the manufacture of polyurethane elastomeric fibers. In our synthesis program we used both polyester and polyether. (See Section IV.) Types that are commercially available include the following:

(1) duPont Lycra (Polyether): This product results from the reaction of polytetramethylene glycol (1000 molecular weight) with TDI to form a hydroxy-terminated diol. This diol is reacted with MDI to form an isocyanate terminated adduct. The adduct is then reacted with hydrazine in dimethyl formamide to form a polymer which contains both urea and urethane groups. The polymer is in solution and wet spun to form the final fiber.

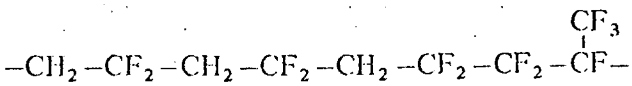
(2) Uniroyal Vyrene (Polyester): This product results from the reaction of adipic acid with a mixture of polyethylene and polypropylene glycols to form a polyester diol. The diol is reacted with MDI to form a prepolymer which is isocyanate terminated. The prepolymer is extruded into an ethylene diamine bath and cured in a two-step curing process.

(3) Carr Fulflex Carrlastic (Sulfur Cured Polyester): This product results from the same reaction outlined for Vyrene, except that a portion of the acid is unsaturated. After the isocyanate-terminated polyester is formed, amine is added and the product is heated until a high-molecular-weight prepolymer is formed that can be handled on conventional rubber processing equipment. Sulfur and other curing agents are added and the product is calendered to give a sheet that is then cut into thread.

In the additive program we worked with two commercial products, duPont's Lycra and B. F. Goodrich's Estane as well as one of our synthesized products. These were dissolved in dimethylformamide and the various additives incorporated into the solution. This solution was used either to cast a film or to spin fibers.

3. Fluorocarbon Elastomers

The materials used in this program were copolymers of vinylidene fluoride and hexafluoropropylene having the approximate formula:



$$-CH_2-CF_2-CH_2-CF_2-CH_2-CF_2-CF_2-\overset{CF_3}{\overset{|}{C}}F-$$

These polymers are produced only by 3M Company and E. I. duPont de Nemours & Co., Inc., under the trade names Fluorel and Viton, respectively. These fluoro elastomers are known for their outstanding heat, fluid, and flame resistance. They have been used by NASA as a nonflammable elastomeric material in 100% oxygen environments. However, they have poor recovery properties. Since they are compatible with Spandex urethanes, and soluble in solvents used for Spandex (DMF), and the combination can be spun into fibers; we used the fluorocarbon in combination with urethane.

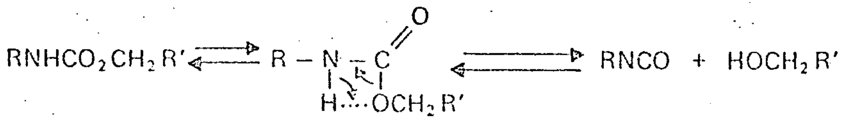
B. FIRE RETARDANCY

1. Urethanes

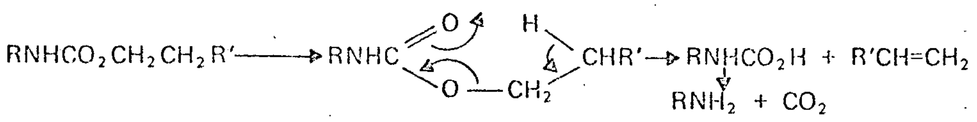
Only a limited amount of work (other than NASA) has been done to improve the flame resistance characteristics of flexible urethanes, and only to meet the relatively mild requirements of a tunnel test. However, the use of 100% oxygen atmospheres, along with a relatively long ignition (a silicone ignitor), presents most severe conditions, and conventional flame resistant materials will burn in this type of environment. The burning of urethane film or fiber can be considered a three-stage process: The initial heating of polymer, decomposition of the polymer, and ignition.

When Spandex type polyurethane starts to burn, the urethane structure breaks down to form a variety of end products, depending on flame temperature and the amount of oxygen present. Figure 1 shows the primary modes of urethane decomposition and the end products that are expected to be formed. These include many particularly flammable end products such as alcohols, olefins, and isocyanates. These end products break down further in the oxygen enriched atmosphere and form a variety of substances, including water, hydrogen, methane, CO, and CO_2.

1. Retro Fission into Isocyanate and Alcohol



2. Decomposition to Primary Amine, Olefin, and CO_2



3. Decomposition to Secondary Amine and CO_2

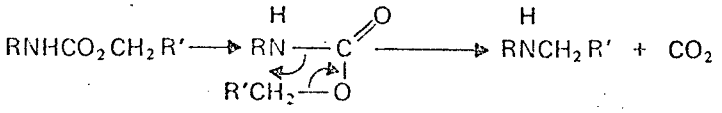


FIGURE 1 PRIMARY MODES OF URETHANE DECOMPOSITION

2. Halogens

The inhibiting effects of halogens or hydrogen halides on the combustion of different materials have been widely studied, but the exact mechanism by which they impart flame retardancy is not clear. It is generally agreed, however, that part of the effect is that the halogen atom retards and inhibits the burning by terminating the free-radical combustion chain reaction in the gaseous phase. (See Figure 2.) This view is supported by the fact that much of the halogen in the halogen-containing polymer is converted to the hydrogen halide during decomposition. The hydrogen halide is regenerated by further reaction of the halogen liberated with the fuel. Thus, in the inhibition reaction and regeneration reaction in the second stage of the burning process, the hydrogen halide alters the mechanisms of the pyrolytic polymer decomposition and changes the amount and the flammability of the volatile gases produced.

It is also believed that halogens function by capturing electrons and thus preventing the activation of the oxygen to the ionic form needed for combustion.

The effectiveness of the halogen species increases in the order of fluorine, chlorine, bromine, and iodine. This effectiveness can be related directly to the bond dissociation energies of the halogens. (See Figure 3.) Obviously, the iodine materials should be the most effective, but they are too unstable to be practical.

Initiation of Combustion

$$\text{Polymer (fuel)} \xrightarrow[\text{heat}]{O_2} R\bullet + \bullet OH + H\bullet + CO + CO_2 \text{ etc.}$$

Propagation

$$\bullet OH + CO \longrightarrow CO_2 + H\bullet \quad \text{Exothermic}$$
$$H^{\circ} + O_2 \longrightarrow \bullet OH + O\bullet$$

Inhibition

$$\bullet OH + HBr \longrightarrow H_2O + Br\bullet \quad \text{A lower-energy process}$$
$$H\bullet + HBr \longrightarrow H_2 + Br\bullet$$

Regeneration:

$$\bullet Br + RH \text{ (fuel)} \longrightarrow HBr + R\bullet$$

FIGURE 2 MECHANISM OF INHIBITION OF COMBUSTION BY HALOGEN-CONTAINING FLAME RETARDANTS RADICAL-CHAIN PROCESS

H–F	135.8	H–Br		H–C	81-104
H–Cl	103.0	H–I	71.3	H–O	102.4

FIGURE 3 BOND DISSOCIATION ENERGIES, Kcal/mole

III. SAMPLE PREPARATION AND TESTING PROCEDURES

A. SAMPLE PREPARATION

To make our test samples, we prepared a dope or solvent solution of the urethane and the various compounding ingredients. This dope was used to either cast a film or spin fibers. In a typical procedure, duPont Lycra Spandex fiber was chopped to about 1/2 inch length. This chopped fiber was added slowly, with constant stirring, to dimethylformamide to give a 15% solution of Spandex fiber. The various additives were incorporated into the solution, the solution was ball milled overnight to assure good uniformity and dispersion, and it was then filtered through cheesecloth to remove any gelled particles. The filtered solution was cast on glass plates to give a wet film about 15 mils thick. This film was dried at 80°C (176°F) for three hours, stripped from the glass plate, and dried in a vacuum oven at 80°F for one hour. The dried film was about 5 mils thick.

In making the fibers, we used the same filtered solution but pumped it through a 40-end spinneret, and dropped it into a water bath at about 120°F to precipitate the fiber. The fiber was run along a length of water bath to remove solvent, through nip rolls to coalesce the fibers and remove excess water, and finally through an oven at 190°F to dry.

The thickness of a film or fiber influences its flammability; for example, "Refset" films less than 50 mils thick will burn in 100% oxygen. In order to evaluate the effect of thickness with urethanes, we prepared compounds using Estane (a thermoplastic urethane) and hexabromobenzene (HBB). Formulations contained 30% Estane and 70% hexabromobenzene. As shown below, the oxygen index drops off to 50 as the thickness of the specimen is reduced from 50 mils to 15 mils.

Test Film* Thickness (Mils)	Oxygen Index
80	75
50	75
25	65
15	50

*Formulation No. 44-71, 30% urethane and 70% HBB.

This decrease clearly points out that any flame-retardant system developed for fibers or thin films must have substantially better flame resistance properties than a system for thick sections. For example, many formulations that we have developed have good physical properties but 5-mil specimens of these formulations will not pass the 100% oxygen test.

Commercially available Spandex fibers, for example, are as much as 15 mils thick. On the project this was the minimum we worked with. Occasionally we worked with fibers up to 25 mils thick.

B. TESTING PROCEDURES

1. Oxygen Index

Flammability of the samples was tested by the oxygen-index method (tentative ASTM method, May 14, 1969). In this test, the oxygen index, N, of a material is the percentage concentration of oxygen in a mixture of oxygen and nitrogen at atmospheric pressure that will maintain equilibrium burning conditions. Physically, this percentage is the lowest concentration of oxygen that will support sustained combustion of the material and is computed according to the formula:

$$N = \frac{100\,[0_2]}{[0_2] + [N_2]}$$

where $[O_2]$ is the oxygen concentration at equilibrium and $[N_2]$ is the associated nitrogen concentration. Thus, the smaller the value of N, the more flammable the specimen.

In this test, a film sample of the material 7-15 cm long x 6.5 ± 0.5 mm wide x 0.025-0.01" thick was placed vertically in the center of a column; the column was filled with gases flowing at a rate of 5 cm/sec and ignited by a hydrogen flame.

Normally, measurements made by this method involve igniting the sample at the top. In this investigation, we modified this method and burned the sample in the selected atmospheres at the bottom of the specimen strip. Two samples were used for each test. The reproducibility of this method is ± 1.

This test was designed to overcome, as far as possible, the three major drawbacks of a number of flammability tests: (1) the manner in which the sample is ignited; (2) the definition of the end point; and (3) operation under nonequilibrium conditions.

A schematic diagram of the test apparatus is shown in Figure 4.

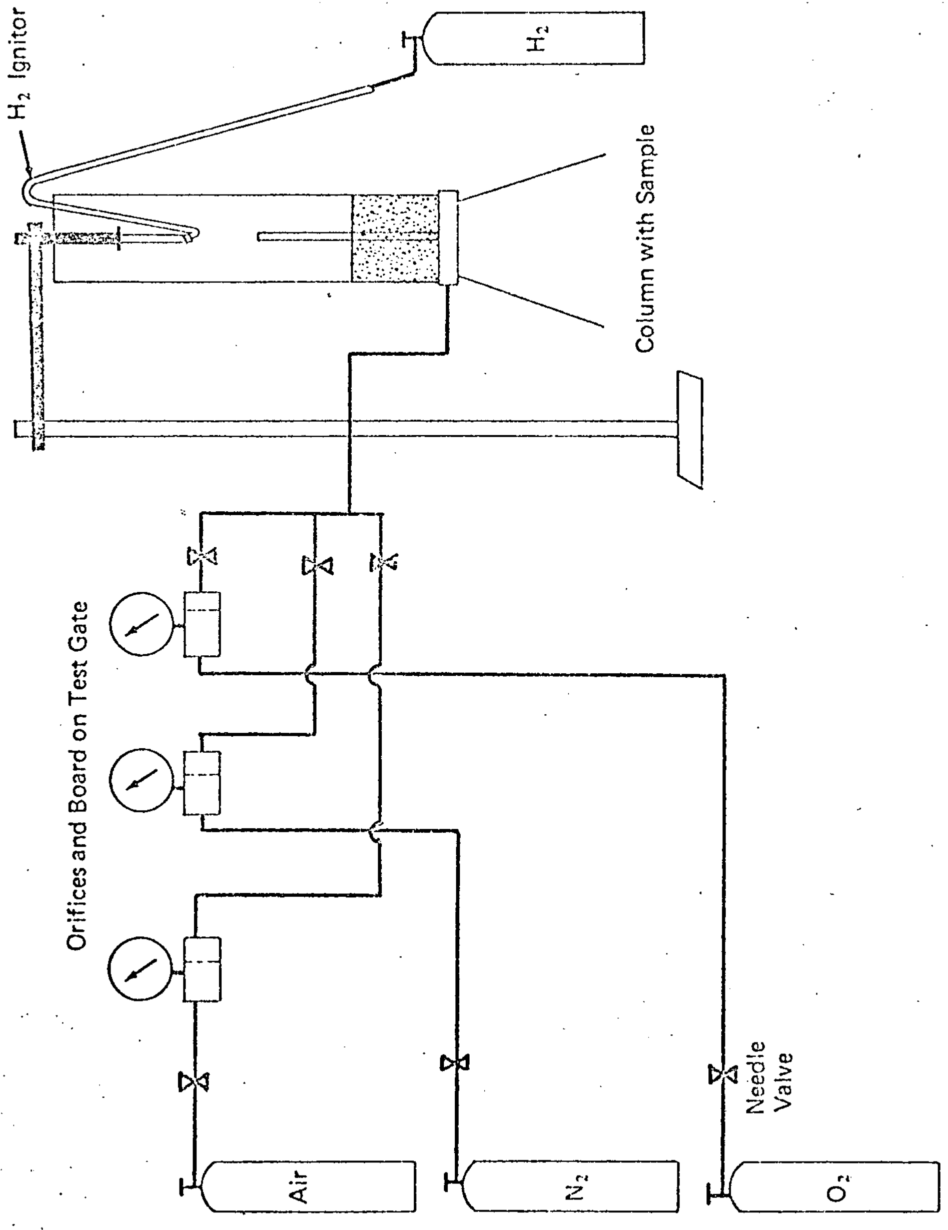


FIGURE 4 OXYGEN INDEX APPARATUS

2. Effect of Revised Test Procedure on Sample's Oxygen Index

In our original procedure, we recorded the value when the specimen stopped burning but ignored whether any material that dropped off was still burning. In the revised test, the specimen extinguishes itself and any burning material that drops off stops burning before it reaches the bottom of the container. The new procedure results in oxygen index values approximately 10 points below the original values; results of both are shown in Table 1.

Tables 1 and 2 compare the tests of materials that were evaluated at NASA and also evaluated by us. It was concluded that to pass the 35 oxygen/65 nitrogen test at 10 psia, a material should have an oxygen index of 45-50 according to our revised test and a halogen content of 65-70%. To pass the 60 oxygen/40 nitrogen test, it should have an oxygen index of 65-75.

3. Physical Properties

Tensile and elongation properties of the formulated elastomer were measured according to ASTM Method 412. The Instron tester was set at a speed of 20"/min and the dumbbell was cut with a die D.

4. Controls of Polymer Synthesis

In order to control our synthesis, we performed as standard procedure the following tests: (a) hydroxyl numbers, ASTM D 1638, (b) acid number, ASTM D 1638, (c) water, ASTM D 1638, and (d) free isocyanate, ASTM D 2572.

5. Materials

A list of materials used in the program and suppliers for them is included in Appendix A.

TABLE 1

FLAME RETARDANCY DATA IN SELECTED SAMPLES

			ADL Test Data					NASA Results		
Report Reference No.	Code #	Flame Retarding Material	% Flame Retardant	% Halogen of Composition	Revised Oxygen Index	Standard Oxygen Index	Comments	Pressure (psi)	Gas (% O_2)	Rate of Propagation (inches/second)
1	27-27	Hexabromobenzene	80	69.6	50-55	70	Fair film not very flexible	10 6.2	35 100	Self extinguishing 0.5
2	27-28	Hexabromobenzene D.B.P.P	44 44	65.0	45	57	Fairly good fairly flexible Bleeds some what	–	–	–
3	27-29	Hexabromobenzene D.B.P.P.	50 40	67.9	45-50	57	Bleeds some what	10	35	0.14
4	27-30	Hexabromobenzene D.B.P.P	30 30	44.4	30	40	Excellent properties	10	35	0.30
5	27-31	Decabromodiphenyl D.B.P.P	55 30	63.1	40	57	Fair to good properties	–	–	–
6	27-32	Decabromodiphenyl D.B.P.P	60 30	67.5	45	59	Fair to good properties	–	–	–
7	27-32a	Hexabromobenzene D.B.P.P	60 30	70.2	45	60	Fair to good properties	–	–	–
8	28-35	Hexabromobenzene B.C.P.P	65 20	68.7		60				
9	28-36	Hexabromobenzene B.C.P.P	60 30	70.5		54.0				
10	28-37	Hexabromobenzene B.C.P.P	68 20	72	55	62.0		10 6.2	35 100	Self extinguish 0.75

*D.B.P.P = Tris-2,3-dibromopropyl phosphate
*B.C.P.P = Tris-1-Bromochloropropyl phosphate

TABLE

PHYSICAL PROPERTIES AND FLAME RES

Code #29-	38	39	40	41	42	43	44	45
% Spandex	10	10	10	10	20	20	20	20
% Hexabromobenzene	45	55	65	75	40	48	56	64
% Tris-bromochloro-propylphosphate	45	35	25	15	40	32	24	16
Halogen Content, %	67.5	69.5	72.5	74.5	59.5	61.5	63.5	67
Oxygen Index								
1 Revised	40-50	45-50	50-55	55-60	35-40	40-45	–	40–
2 Standard	55	57	68	65-68	45-48	55-60	55	55-
NASA Flammability Tests								
Burning 35% O_2-10 psi		SE			SE	SE	SE	
Burning 100% O_2-6.2 psi		1.66			1.0	1.25	1.42	
Tensile Strength PSI	373	335	277	310	1157	918	560	727
Elongation %	600	563	500	125	625	638	600	48

Control - Spandex Alone

Oxygen Index - 19
Tensile PSI - 7100
Elongation % - 700

TABLE 2

FOLDOUT FRAME 2

ES AND FLAME RESISTANCE OF SPANDEX COMPOUNDS

44	45	46	47	48	49	50	51	52	53	35-1
20	20	40	40	40	40	50	50	50	50	5
56	64	30	36	42	48	25	30	35	40	68
24	16	30	24	18	12	25	20	15	10	27
63.5	67.0	44.6	46.2	48.0	49.1	37.2	38.5	39.8	41.1	76
–	40-45	35	35-40	30	30	25-30	25-30	25-30	30-35	60-65
55	55-60	42	47	47	37	35	37	32	42	68-70
SE			0.71							SE
1.42			1.66							1.25
560	727	1750	1905	1657	1726	3090	2625	2994	2956	–
600	488	713	650	563	575	713	675	650	675	–

IV. SYNTHESIS OF URETHANE POLYMERS

The physical properties of two control urethanes, prepared from a hydroxy-terminated polyester and polyether, are shown in Table 3. A list of other products (together with the reactants used) is given in Table 4.

TABLE 3

CONTROL URETHANES

	Polyether	Polyester
Trade Name	Polymeg 1000	Formney L8-71
Company	Quaker Oats	Witco
Molecular Weight	1500	1900
Hydroxyl No.	74.9	60.6
Polyurethane Properties		
Elongation %	500	800
Tensile psi	4500	6400

The highlights of the synthesis program are given below under the heading of the key halogenated monomer involved. (See Appendix B for chemical structure of reactants and products.)

A. POLYETHER AND POLYESTER URETHANES (APPENDIX B; 1A, 1B)

The optimum molecular weight for a base diol is 2,000-5,000; however, diols with a molecular weight of 1,000 can be used if they are first reacted with TDI – 1 mole diol to 1/2 mole TDI – to form the required 2,000 molecular weight base diol. This procedure was followed with the polyether (molecular weight 1,000) but not for the polyester since the polyester's molecular weight was 2,000.

Spandex urethane was prepared by reacting the diol with MDI (1:2 mole ratio) to form an isocyanate-terminated prepolymer which was then extended to a linear, high-molecular-weight molecule soluble in DMF.

TABLE 4

SUMMARY OF POLYMER SYNTHESIS PROGRAM

Code No. Appendix B	Starting Materials	Products
1-A	Polyether urethane Polymeg 1000 Quaker Oats treated with TDI	Control formulation. Properties standard for Spandex. Oxygen index 20.
1-B	Polyester urethane Polybutyl adipate treated with TDI	Control formulation. Properties standard for Spandex. Oxygen index 20
2-A	Dibromoneopentyl glycol (Dow SA 1138) treated with adipic acid, TDI, and hydrazine	Oxygen index 32. Crosslinks excessively during reaction leading to gelled product
2-B	Dibromoneopentyl glycol (Dow SA 1138) treated with TDI, and with polybutyl adipate	Oxygen index 23, tensile strength 4,000, elongation 300%
3-O	HET acid (Durez Chemical) treated with butanediol	Brittle solid
4-A	PHT4-diol (Michigan Chemical) treated with adipic acid and MDI	slightly flexible and brittle Oxygen index 35
4-B	PHT4-diol (Michigan Chemical) treated with azelaic acid	Slightly elastomeric. Oxygen index 28
4-C	PHT4-diol (Michigan Chemical) treated with dimer acid and MDI	Very soft, poor recovery oxygen index
4-D	PHT4-diol (Michigan Chemical) treated with azelaic acid and hexamethylene diisocyanate	Very soft and weak
5-O	Tetrabromophthalic anhydride treated with butanediol	Liberates HBr during esterification (not used)
6-O	Butenediol. Treated with adipic acid, brominated and treated with MDI and hydrazine	Final product not stable on storage
7-O	Trans-2-,3-dibromo-2-butene-1-,4-diol (Aldrich Chemical) treated with adipic acid	Viscous liquid, black, unstable
8-O	Butenediol treated with dibromoadipic acid	Liberated HBr and degraded during esterification
9-O	Perfluoroglutaric acid. Treated with 2,2,3,3,4,4-hexafluoro-1-,5-pentanediol	Degraded during esterification
10-O	Halogenated polyether (Swift CH 940-321) treated with TDI, MDI, and hydrazine	Slow reaction, waxy product
10-O	Halogenated polyether (Swift CH 940-341) treated with TDI, MDI, and hydrazine	Slow reaction, waxy product
10-O	Halogenated polyether (Swift CH 940-371) treated with TDI, MDI, and hydrazine	Slow reaction, waxy product (no improvement over above two materials)

B. DOW SA 1138 WITH ADIPIC ACID (APPENDIX B; 2A)

DOW SA 1138 is a brominated neopentyl glycol containing 61% bromine by weight. A polyester polyol was prepared by reacting the SA 1138 with adipic acid in the presence of a Tyzor TPT catalyst. The reaction was carried out in a glass/Teflon system with a nitrogen purge.

During the polyester formation, at 160-190°C, HBr was constantly given off and appeared mainly in the product water as long as the reaction was proceeding at a reasonable rate. The reaction was completed using both heat and vacuum. Acid numbers were usually 3 to 6 and unreacted glycol could be seen subliming in the cool vacuum lines at the end of each reaction during the vacuum stripping step.

All attempts to prepare MDI prepolymers from SA 1138 adipates at 80-90°C resulted in the formation of gels insoluble in DMF. A dry strip of gel had an oxygen index of 33. A soluble prepolymer was finally prepared by reacting the SA 1138 adipate at room temperature with MDI. However, a DMF insoluble gel resulted during the chain extension step when the prepolymer was added to a DMF solution of hydrazine. The dry gel was hard and brittle.

A similar chain extension step was conducted using a technical grade of ethylene glycol, mainly to determine whether hydrazine was causing dehydrohalogenation (thereby producing an oxetane ring which on opening could cause crosslinking and gelation). Ethylene glycol also resulted in a DMF insoluble gel, showing that hydrazine alone was not causing the gel.

Using a standard $AgNO_3$-HNO_3 solution, we made qualitative tests to determine whether any detectable amount of HBr was present in the SA 1138 adipate gels; none was found.

We believe there are two possible explanations for the gel formation:

(a) The presence of trifunctional impurities in the SA 1138.

(b) Side reactions when HBr splits out during polyester preparation and provides sites for crosslinking during the reaction with TDI or MDI.

Attempts to prepare the polyester by reaction with adipic acid at lower temperatures (77°C for 16 hours) resulted in a reaction that was 80% complete. Despite the mild conditions the extended product was sufficiently crosslinked to give an insoluble gel in dimethylformamide. We decided to terminate ester synthesis with this monomer. In one case, however, we treated the glycol itself with MDI and then extended it with hydrazine. A clear brittle film was formed that has an oxygen index of 24 (versus 19 for regular Spandex). This result suggests that the second explanation for the gelation may be the most plausible one.

C. DOW SA 1138 WITH TDI (APPENDIX B; 2b)

Dow SA 1138 (brominated neopentyl glycol) was treated with TDI (1:2 mole ratio) and the isocyanate-terminated product was then reacted with the polyester from butanediol and adipic acid, thus introducing 9.5% bromine into the polymer chain. The product has physical properties similar to those of Spandex and an oxygen index of 25. This reaction appears to be a convenient way to improve the flame resistance slightly (an increase of 5 points over Spandex), which is adequate to offer protection in air. This level of flame resistance could be of interest in a number of commercial applications.

D. HET ACID (APPENDIX B; 3)

A polyester was prepared using HET acid and butanediol. The reaction was kept below 190°C with a nitrogen purge (as per Durez recommendations). The product was a dark brown brittle solid that was soluble in THF. Because the product was brittle and not suitable for use as a flexible fiber, work on this material was discontinued.

E. PHT 4-DIOL (APPENDIX B; 4)

This material is the reaction product of brominated phthalic anhydride and ethylene and propylene oxides. It has given the most promising results so far.

1. Reaction with Adipic Acid (Appendix B; 4a)

An adipate was prepared having an acid number of 6.83 and a hydroxyl number of 41.4. No HBr was evolved during the reaction, indicating that the molecule is quite stable. The prepolymer was prepared with MDI and extended with hydrazine to give a dry film – strong, hard, flexible and clear – with an oxygen index of 30.

2. Reaction with Azelaic Acid (Appendix B; 4b)

In order to increase the flexibility, our next step was to react the PHT 4-diol with azelaic acid to provide a longer chain. The polyester was then terminated with MDI and extended with hydrazine. This product was somewhat more flexible, but still too brittle for use.

3. Reaction with Dimer Acid (Appendix B; 4c)

In order to attain more flexibility, we treated the PHT 4-diol with dimer acid to form a polyester. It was then reacted with TDI and extended with hydrazine. The resulting product was extremely soft. Apparently it did not have sufficient chain length, and it was not acceptable as a fiber-forming material.

4. Reaction with Azelaic Acid and HDI (Appendix B; 4d)

This reaction was the same as with azelaic acid, except that hexamethylene diisocyanate was used in place of MDI in hopes of obtaining a more flexible product. The product was very soft and weak and not as satisfactory as urethane with azelaic acid and MDI.

F. TETRABROMOPHTHALIC ANHYDRIDE (APPENDIX B; 5)

Tetrabromophthalic anhydride was reacted with butanediol to form a hydroxy-terminated polyester. The product was unstable and could not be used for further work.

G. BROMINATION OF BUTENEDIOL-ADIPIC ACID POLYESTER (APPENDIX B; 6)

We prepared an unsaturated polyester by the reaction of 2-butene-1,4-diol and adipic acid (1.19:1 mole ratio). The resulting polyester had the following properties:

Appearance	Tan, waxy solid
Acid Number	12.1
OH Number	67.1
Average M.W.	1,400

A solution of the polyester was prepared in methylene dichloride (13%) and cooled to -30°C. Bromine dissolved in methylene dichloride was added slowly to the polyester in the dark; the product was neutralized, washed, and the solvent evaporated. The polymer was then reacted with MDI and extended with hydrazine. The resulting product had an oxygen index of 32. When a film of the material was first cast, it had reasonably good physical properties, but these deteriorated over a two- or three-day period. If a sample is enclosed in a container with wet litmus paper inserted, the paper becomes red indicating the liberation of HBr. We concluded that the compound is unstable at room temperature and gradually breaks down and liberates bromine. This approach was discontinued.

H. 2,3-DIBROMO-2-BUTENE-1,4-DIOL-ADIPIC ACID (APPENDIX B; 7)

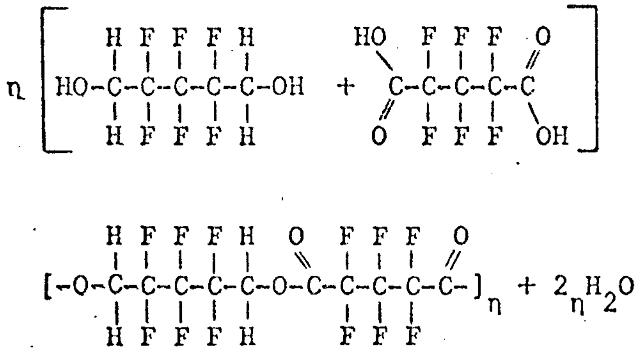
We prepared an unsaturated polyester by treating adipic acid with 2,3-dibromo-2-butene-1,4-diol in the hope that a polyester could be made that could be further reacted to form a urethane with an available double bond for bromination. A hydroxy-terminated polyester could not be formed because HBr evolved during the esterification.

I. DIBROMOADIPIC ACID BUTANEDIOL POLYESTER (APPENDIX B; 8)

This material was treated with polypropylene glycol. During synthesis HBr was evolved and the product was a black liquid. Work on this material was terminated.

J. PERFLUOROGLUTARIC ACID-2,2,3,3,4,4-HEXAFLUORO-1,5-PENTADIOL (APPENDIX B; 9)

An attempt was made to prepare a hydroxy-terminated polyester from perfluoroglutaric acid and hexafluoropentanediol using 1.2 moles of diol to 1 mole of the diacid. The reaction yielded a light waxy amber-colored product with a very high acid number. Attempts to neutralize the excess acid resulted in what appeared to be hydrolysis of the polyester, since perfluoroglutaric acid is a very strong acid and would be expected to form an easily hydrolyzed polyester. The chemical structure of the two materials and that of the reaction product are:



The properties of the acid, diol, and resulting polyester are as follows:

	Acid	Diol	Polyester
Molecular Weight	240	212	
Melting Point °C	78-88	77.5	
Weight % Fluorine	47.5	53.7	
Acid Number			134
Hydroxyl Number			
Flammability (Oxygen Index)			30

K. SWIFT POLYETHERS (APPENDIX B; 10)

Three halogenated polyethers from Swift – treated with TDI, MDI, and extended with hydrazine – gave products that were waxy and gummy. The unreacted diols were quite dark and low in viscosity, most likely indicative of impurities and a low molecular weight, respectively.

The three Swift samples have the following composition:

	CH 940-321	CH 940-341 H	CH 940-371
OH No.	85.2	40.0	66.8
Acid No.	0.1	0.1	0.1
% Br	41.3	46.2	38.3
% P	3.06	2.82	2.6

V. ADDITIVES

To establish a starting point for our work and to determine the type of additives that would be effective, we prepared a series of Spandex films that contained a variety of different flame retardants. The casting solution (dope) was prepared by dissolving Spandex in DMF, then adding the retardant in the desired concentrations. Details of the preparation are described in Section III.

A. PRELIMINARY SCREENING OF FLAME RETARDANTS

In this preliminary screening of flame retardants, we used two types of flame retardants: (1) those which are soluble in dimethylformamide (DMF) and (2) those which are insoluble. For the solid flame retardants we determined the oxygen index of the flame retardant alone (without using Spandex) and mixed with varying amounts of Spandex. Insoluble flame retardants were incorporated into Spandex solution by grinding in a ball mill.

1. Screening of Flame Retardants Without Spandex

Table 5 lists the flame retardants and halogenated polymers which were evaluated without Spandex, the percent halogen and/or phosphorus content of each, and the oxygen index. The conclusion that can be drawn from Table 5 is that bromine is a more effective flame retardant than chlorine or fluorine at a given weight concentration. Figure 5 shows the change in oxygen index versus halogen content. The rapid change in the slope of the curve and the jump in oxygen index between 60% and 80% halogen content defined this level as the point of major interest in this program. For the 100% oxygen environment a halogen content of at least 80% should be used.

2. Flame Retardants With Spandex

These materials were incorporated into a urethane spinning dope and a film cast to give a dry film 5 mils thick. The resulting film was dried and tested for stress-strain characteristics and flame retardancy.

Physical properties and oxygen index values for the compounds are reported in Table 6.

a. Soluble Additives

- Good flame retardancy, fair physical properties: tris-2,3-dibromopropyl phosphate and tris-1-bromochloropropyl phosphate.

TABLE 5

OXYGEN INDEX OF HALOGENATED MATERIALS ALONE

Material	% Halogen Content	Oxygen Index
Brominated		
Tetrabromoethylene aniline	76.0	70
Hexabromocyclododecane	74.5	45
Hexabromobenzene	87.0	100
Decabromodiphenyl	82.0	100
Chlorinated		
Polyvinylchloride	56.5	42
Dechlorane Plus 25	65	50
Polyvinylidenechloride	72	53
Hexachlorobenzene*	75	100
Fluorinated		
Polyvinylfluoride	41	23
Polyvinylidenefluoride	59	32
Tetrafluoroethylene	76.5	65

*sublimes

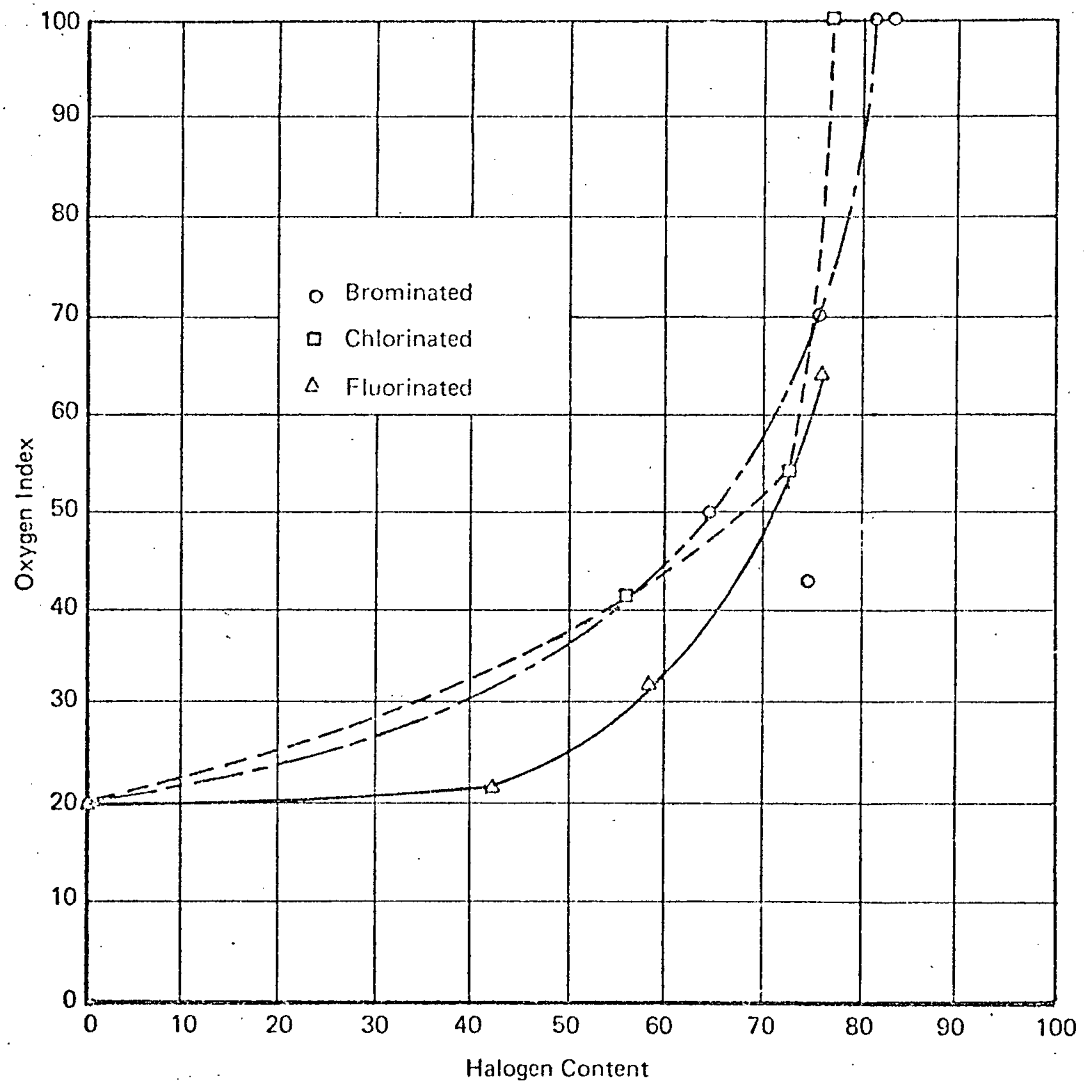


FIGURE 5 EFFECT OF HALOGEN CONTENT OF FLAME RETARDANT (ALONE) ON OXYGEN INDEX

TABLE 6

PHYSICAL PROPERTIES AND OXYGEN INDEX FOR SPANDEX COMPOUNDS

Report Reference No.	Code No.	Materials	%	% Halogen	Oxygen Index	Tensile Strength	% Elongation	Comments
				Soluble Type				
1	2-3	tris-2,3-dibromopropyl phosphate	16.66	11.6	25	3421	667	
2	2-3a	tris-2,3-dibromopropyl phosphate	33.33	23.2	28	2916	788	
3	2-4	tetrabromoethane (acetylene tetrabromide)	16.66	14.7	22	3990	606	
4	2-4a	tetrabromoethane (acetylene tetrabromide)	33.33	29.4	24	5087	675	
5	2-5	tris-1-bromochloropropyl phosphate	16.66	10.1	24	2725	650	
6	2-5a	tris-1-bromochloropropyl phosphate	33.33	20.2	23	2180	720	
7	2-7	2,3-dibromopropanol	16.66	12.0	22	2170	557	
8	2-7a	2,3-dibromopropanol	33.33	24.0	24	2437	550	
9	11-20	tris β-chloroethylphosphate	50	18.3	28	–	–	Fair film
10	11-22	phosgard 22R[a]	50	11.0	23	–	–	Poor film
				Insoluble Type				
11	2-2	RF 272[b]	16.66	–	24	2435	626	Poor film
12	2-2a	RF 272	33.33	–	25	502	313	Poor film
13	2-6	Dechlorane plus 25[c]	16.66	10.5	24	2110	350	Poor film
14	8-3	Tetrabromobisphenol A	16.66	9.5	22	2526	800	
15	8-4	Tetrabromobisphenol A	33.33	19.0	25	1800	800	
16	8-5	Tetrabromobisphenol S	16.66	9.4	20	2823	700	
17	8-6	Tetrabromobisphenol S	33.33	18.8	21	2300	560	
18	9-7b	Hexabromobenzene	34.0	29.2	25	–	–	Good film
19	9-15	Tetrabromobutane	33.33	28.6	27	–	–	Fair film
20	9-16	Carbon tetrabromide	33.33	31.5	24.0	–	–	Poor film
21	11-23	Ammonium phosphate	50	–	23.0	–	–	Fair film
22	11-24	Ammonium phosphate	80	–	36.0	–	–	Poor film

[a] Organophosphorous compound made by Monsanto

[b] American Cyanamid halogenated phosphorous containing material

[c] Hooker Chemicals chlorinated cyclic organic material

- Good physical properties, fair flame retardancy: tetrabromoethane (acetylene tetrabromide).

- Poor physical properties and flame retardancy: 2,3-dibromopropanol, tetrakishydroxymethyl phosphonium chloride and tris-β-chloroethyl phosphate.

b. Insoluble Additives

- Good flame resistance: tetrabromobutane has excellent flame retardancy, but a low melting point and poor thermal stability. Hexabromobenzene has good flame resistance along with good thermal stability and is therefore a preferred material.

Ammonium phosphate alone has an oxygen index of 100%, but when mixed with Spandex it was not effective.

Based on the above, we selected hexabromobenzene and tris-2,3-dibromopropyl phosphate as the most promising materials. These and others were incorporated into Spandex at different levels to evaluate flame retardancy characteristics, compatibility, and physical properties of the compounds. The effects of each additive are:

- Hexabromobenzene (see Table 7): As the percent of hexabromobenzene increased the oxygen index values also increased; that is, oxygen index was proportional to the amount of halogen in the system. Films containing 92% hexabromobenzene (the amount required to get the 100% oxygen index) were very stiff and brittle. Halogen content was 80%.

- Tris-2,3-dibromopropyl phosphate (see Table 8): As the percent of tris-2,3-dibromopropyl phosphate increased, the oxygen index increased. The change was less than with hexabromobenzene, however, because halogen content was lower (67%). The material acts as a plasticizer but tends to bleed out of the compound at levels higher than 25%.

TABLE 7

EFFECT OF CHANGING % OF HEXABROMOBENZENE ON OXYGEN INDEX

Report Reference No.	Code No.	% HBB in Spandex	% Br Content	Oxygen Index
1	10-19	92	80.0	100
2	9-17	80	70.0	54
3	9-17a	57.5	50.0	45
4	9-17b	50	43.5	28.0
5	9-7b	34	29.0	26.0

TABLE 8

EFFECT OF CHANGING % OF DBPP ON OXYGEN INDEX

Report Reference No.	Code No.	Material	%	% Bromine	Oxygen Index	Comments
1	2-3	Tris-2,3-dibromopropyl phosphate	16.66	11.6	24	
2	2-3a	Tris-2,3-dibromopropyl phosphate	33.33	23.2	28	
3	10-18	Tris-2,3-dibromopropyl phosphate	59	40.0	37	Tris-2,3-dibromopropyl phosphate bleeds out from film
4	10-18a	Tris-2,3-dibromopropyl phosphate	77	52.5	40	Tris-2,3-dibromopropyl phosphate bleeds out from film

B. TWO-COMPONENT SYSTEMS

In an attempt to develop a compound with the optimum combination of physical properties and flame resistance, we worked with two-component systems containing 33 to 66% flame retardant material, based on the Spandex. The results are shown in Table 9. Of these, the most interesting were:

> tris-2,3-dibromopropyl phosphate and hexabromobenzene or decabromodiphenyl behave about the same (formulation #4, Table 9), using HBB had good flame resistance and fair physical properties.

Those with the best physical properties but poor to fair flame resistance were:

> tetrabromomethane,
>
> acetylene tetrabromide and hexabromobenzene, and
>
> tris-2,3-dibromopropyl phosphate and tetrabromo acetylene tetrabromide.

The total concentration and percentages of the flame retardant components were varied in the more promising systems (Table 1): hexabromobenzene with tris-2,3-dibromopropyl phosphate and decabromodiphenyl, tris-1-bromochloropropyl phosphate.

At the same concentration mixtures of hexabromobenzene and tris-2,3-dibromopropyl phosphate were more effective than decabromodiphenyl and tris-2,3-dibromopropyl phosphate or mixtures of hexabromobenzene and tris-1-bromochloropropyl phosphate. On storage the tris-2,3-dibromopropyl phosphate bleeds out when used at levels higher than 25% so the tris-1-bromcchloropropyl phosphate must be used.

1. Tris-1-bromochloropropyl Phosphate

Because tris-2,3-dibromopropyl phosphate "bleeds out" from Spandex, tris-1-bromochloropropyl phosphate was evaluated at different levels with hexabromobenzene. Oxygen indices and physical properties are shown in Table 2. Selected samples were sent to NASA for evaluation and these results are also shown in Table 2. Figure 6 shows the relationship of oxygen index to halogen content. The curve shows a sharp increase in flame retardancy when halogen content is in the 70-80% range. At 80% halogen content the compound will not burn in a 100% oxygen at atmospheric pressure. In order to achieve this 80% halogen concentration it was necessary to make the formulation 92% hexabromobenzene. Figure 7 shows how the tensile strength is reduced as the loading of flame retardant is increased.

TABLE 9

PHYSICAL PROPERTIES OF SPANDEX WITH TWO-COMPONENT SYSTEMS

Report Reference No.	Code No.	Materials	%	% Halogen	% Phosphorous	% Other Flame Retardants	Oxygen Index	Tensile Strength (psi)	% Elongation	Comments
1	8-1	Tris-1-Bromochloro-propyl phosphate Antimony oxide	25 25	15.3	1.1	21	23.0	1220	540	
2	8-2	Tris-1-Bromochloro-propyl phosphate Antimony oxide	33.33 33.33	20.3	3.6	28	23.0	916	660	
3	8-7	Tris-2,3-dibromopropyl phosphate Hexabromobenzene	10.66 16.66	25.9	0.9		25.0	1850	700	
4	8-8	Tris-2,3-dibromopropyl phosphate Hexabromobenzene	25.0 25.0	39.5	1.3		32.0	1291	660	
5	8-9	Tetrabromoethane (Acetylenetetrabromide Hexabromobenzene	16.33 16.33	29.9			22.0	2040	630	
6	8-10	Tetrabromoethane (Acetylenetetrabromide) Hexabromobenzene	25 25	43.7			25.0	2045	670	
7	9-12	Tris-2,3-dibromopropyl phosphate Tetrabromoethane (Acetylenetetrabromide)	25 25	39.2	1.3		28.0	–	–	Poor film

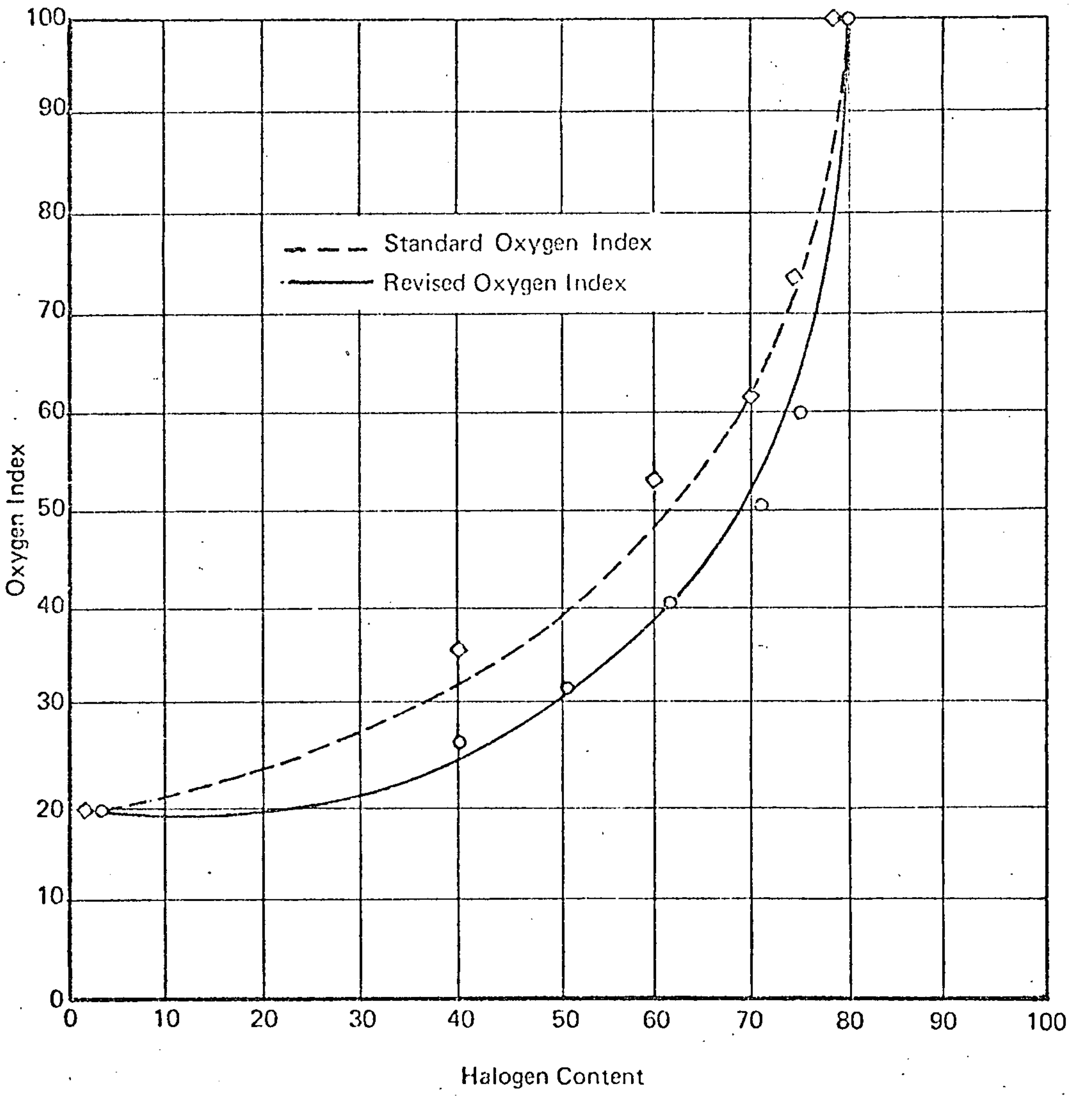


FIGURE 6 RELATIONSHIP BETWEEN STANDARD OXYGEN INDEX AND REVISED OXYGEN INDEX METHOD WITH HALOGEN CONTENT

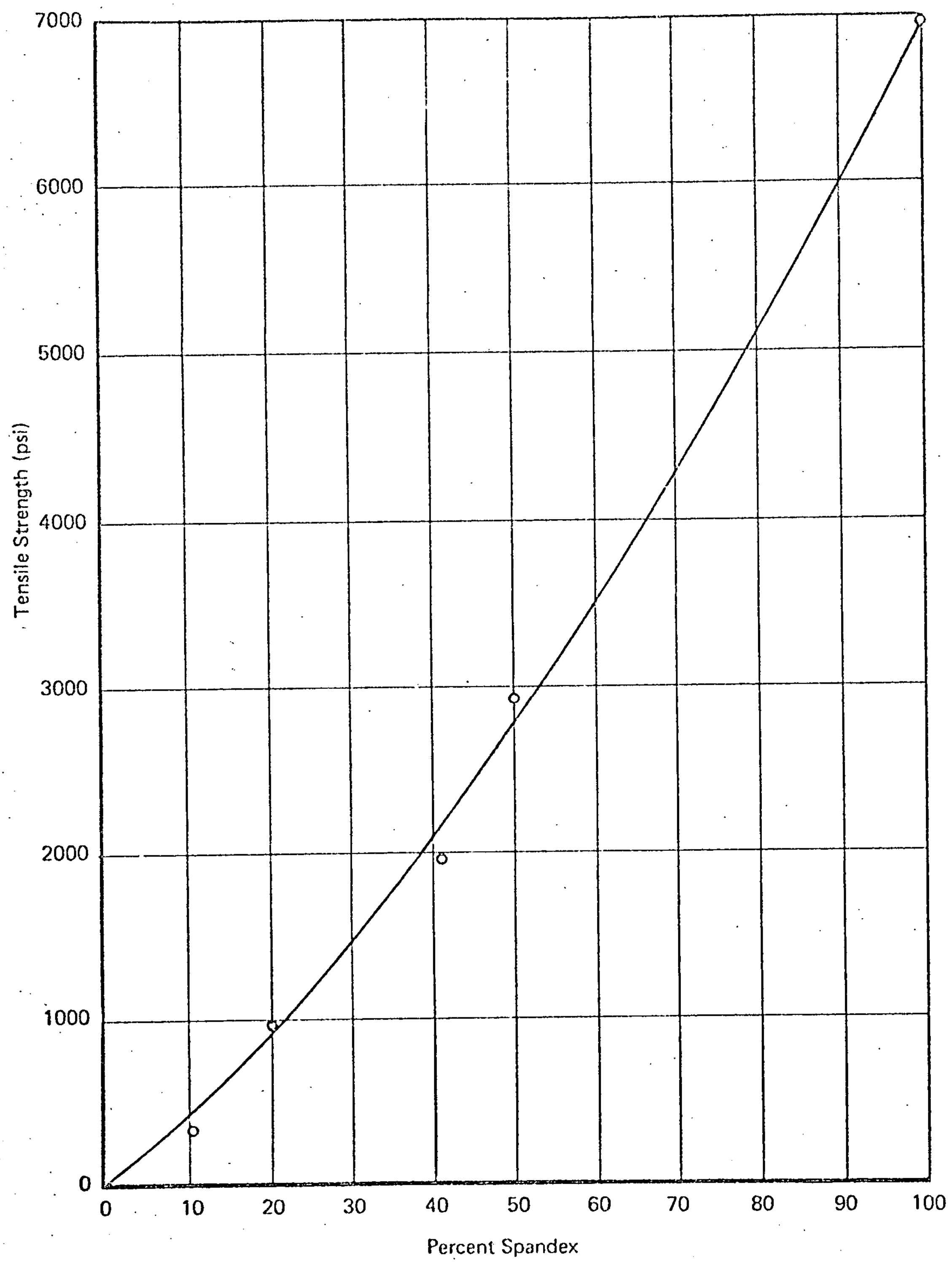


FIGURE 7 EFFECT OF FLAME RETARDANT ON TENSILE STRENGTH

At this stage the effect of using the additives trisbromochloropropyl phosphate and hexabromobenzene to attain a flame resistant Spandex had been fairly well established. Various levels of flame resistance could be achieved, but at a loss of physical properties.

2. Evaluation of Auxiliary Additives for Synergism

To improve the strength characteristics, we examined several systems that might provide a synergistic effect. Combinations that were evaluated included organic halides with metallic oxides, inorganic halides, clays such as Kaolin and blends with fluorine-containing polymers. Our objective was to reduce the concentration of the nonelastomeric content of the compound since this affects the physical properties.

a. Inorganic Halides

Table 10 lists the results with a series of inorganic halides that were added to one of our standard formulations containing hexabromobenzene (HBB) and trisbromochloropropyl phosphate (TBCP). We theorized that these inorganic halides might decompose at temperatures different than the organic halides and thus alter the burning characteristics of the composition. Compositions 1 to 5 contained inorganic halides that apparently have limited solubility in DMF (which is used as a solvent for the Spandex), and these salts caused the Spandex to precipitate; therefore, these samples were not tested. Antimony oxychloride (formulations 6 and 7) could be mixed with Spandex satisfactorily and a film was cast. However, it was not more effective at a given halogen content than a sample containing only hexabromobenzene and trisbromochloropropyl phosphate (formulation 8).

b. Organic Halides

Table 11 lists a series of organic halide-containing compounds that were prepared to determine if they were more effective than the control formulation of hexabromobenzene and trisbromochloropropyl phosphate. Formulations 1 and 2, containing tetrabromoacetylenetetrabromide and carbon tetrabromide, respectively, show these two liquids exert some plasticizing effect. The elongation of these two formulations is better than that of the control. Both materials have a higher halogen content than trisbromochloropropyl phosphate. They may, therefore, be used as effective replacements and be less damaging to physical properties.

TABLE 10

INORGANIC HALIDES AS ADDITIVES

Report Reference No.	Formulation No.	% Spandex	% Organic Halide[1]	Additive	% Additive	% Total Halogen	Oxygen Index
1	48-1[2]	31.8	50	NH_4 Br	18.2	55.0	–
2	48-2[2]	33.7	50	LiBr	16.3	55.0	–
3	48-3[2]	32.3	50	KI	17.7	55.7	–
4	48-4[2]	32.7	50	SbF_3	17.3	48.4	–
5	48-5[2]	32.7	50	$CuCl_2$[3]	17.3	49.9	–
6	51-1	28.6	66.6	SbOCl	4.8	54.0	35
7	51-2	20	47	SbOCl	33.0	52.7	55
8	48-10	30	70	–	–	55.7	35
9	38-61	20	80	–	–	63.3	52

---

1. Percent organic halide (standard ratio) = The percent halogen in the formulation derived from hexabromobenzene and trisbromochloropropyl phosphate added at a 70/30 ratio.

2. These materials cause precipitation of the Spandex when added to the solution.

3. $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$

TABLE 11

PHYSICAL PROPERTIES OF SPANDEX WITH ORGANIC HALIDES

Report Reference No.	Code No.	Percent Spandex	Additive	% Additive	% HBB	% Halogen	Oxygen Index	Tensile Strength (psi)	Elongation (%)
1	41-66	10	Tetrabromo methane acetylene tetrabromide	27.0	63.0	81.2	78	375	250
2	41-67	10	Carbon tetrabromide	27.0	63.0	81.2	72	280	150
3	42-69	10	–	–	90	78.5	78	228	<50
4	47-1	25	Vinyl chloride resin	75	–	43	20		
5	2	50	Vinyl chloride resin	50	–	28.5	20		
6	3	75	Vinyl chloride resin	25	–	14.3	20		

c. Inorganic Oxides

Table 12 lists a series of compounds that were prepared to determine the effect of adding various metal oxides. Of these, cuprous oxide proved to be the most effective. The compounds have better physical properties than the control samples. Table 12 shows a comparison of the compounds on the basis of either total halogen content or Spandex content. Formulations 9 and 10 are controls and contain no metallic oxide. There is evidence of a synergistic effect and further work should be done.

d. Blowing Agents

Since the literature reports that the addition of blowing agents, particularly those containing nitrogen, has an advantageous effect on the flame retardancy of materials when burned in air, we evaluated two of these, azo-bis-formamide and Celogen RA (p-toluene sulfonyl semicarbazide). Both of these materials tended to embrittle the film and neither had any synergistic effect. Table 13 lists the two compounds that were evaluated.

e. Miscellaneous Materials

Table 14 summarizes the results of using auxiliary additives in conjunction with hexabromobenzene and trisbromochloropropyl phosphate. Of these, the most effective was zinc borate, which appeared to have some synergistic effect.

C. FLUORINATED ADDITIVES

A very satisfactory method of imparting flame retardancy to urethanes without seriously detracting from physical properties is to add fluorine-containing elastomeric polymers (Fluorel and Viton) to the hexabromobenzene and Spandex. In all our previous work we had used Spandex. This compound, however, is a relatively high-molecular-weight urethane that has little thermoplasticity. To avoid any solvent entrapment and to enable us to use a hot forming technique we worked instead with Estane, a B. F. Goodrich urethane. Estane (5713) is a thermoplastic fiber-forming urethane that can be mixed on a 2-roll mill and this simplifies sample preparation. (See Table 15.)

Both Viton and Fluorel with hexabromobenzene and no urethane give good flame retardant properties, high oxygen index values (Table 15, 1-3), and good resiliency. Both contain 66.5% halogen.

TABLE 12

OXYGEN INDEX VOLUMES OF SPANDEX WITH METAL OXIDES

Report Reference No.	Code No.	% Spandex	% Organic Halide[1]	Additive	% Additive	% Halogen	Oxygen Index
1	38-55	17	70	Fe_2O_3	13	55.4	45
2	38-56	17	70	PbO	13	55.4	48
3	38-57	17	70	Sb_2O_2	13	55.4	48
4	38-58	17	70	ZnO	13	55.4	38
5	38-59	17	70	TiO_2	13	55.4	42
6	38-60	17	70	Cu_2O	13	55.4	50
7	48-6	28.6	66.5	MgO	4.9	53.1	25
8	48-7	28.6	66.5	NiO	4.9	53.1	38
9	48-11	17.4	82.6	—	—	65.5	50
10	48-12	28.6	71.4	—	—	56.6	45

1. Percent organic halide = The percent halogen in the formulation derived from hexabromobenzene and tris-bromochloropropyl phosphate added at a 70/30 ratio.

TABLE 13

EFFECT OF BLOWING AGENTS IN SPANDEX

Report Reference No.	Code No.	% Spandex	Additive	% Additive	% HBB	% TBCP	% Halogen	Oxygen Index
1	41-68	9.4	Kempore[1]	14.9	85.5		74	72
2	42-69	10		—	90		78.5	78
3	51-5	28.6	Celogen RA[2]	4.8	47.5	19.1	53.1	35
4	51-6	20.0	Celogen RA[2]	33.0	34.0	13.0	36.7	35

1. Kempore (National Polychemicals) Azo-bis-formamide.
2. Celogen RA (UniRoyal) p-toluene sulfonyl semicarbazide.

TABLE 14

EFFECT OF MISCELLANEOUS ADDITIVES ON FLAME RETARDANCY

Report Reference No.	Code No.	% Spandex	% Organic Halide[1]	Additive	% Additive	% Halogen	Oxygen Index
1	49-2	35	60[8]	MDI	5	52.5	28
2	48-10	30	70	–	–	55.7	35
3	48-8[2]	28.6	66.6	Pt[3]	0.025	53.1	–
4	51-3	28.6	66.6	Antioxidant[5]	4.8	53.1	35
5	51-7	28.6	66.6	Cobaltic Acetyl Acetonate	4.8	53.1	30
6	51-9	28.6	66.6	Antioxidant[6]	4.8	53.1	–
7	51-11	28.6	66.6	ZnB_2O_3	4.8	53.1	40
8	49-1	25	60[8]	Carbon black[7]	15	52.2	28
9	48-9	20.0	66.6	Clay[4]	4.8	53.1	35
10	51-4	20.0	47.0	Antioxidant[5]	33.0	36.7	35
11	51-8	20.0	47.0	Cobaltic Acetyl Acetonate	33.0	36.7	20
12	51-10	20.0	47	Antioxidant[6]	33.0	36.1	–
13	51-12	20.0	47	ZnB_2O_3	33.0	36.1	45

1. Percent organic halide – The percent halogen in the formulation derived from hexabromobenzene and tris-bromochloropropyl phosphate added at a 70/30 ratio.
2. When added to Spandex solution causes precipitation because it was deposited on alumina.
3. Platinum (0.5% on alumina).
4. Ultra white 90 (minerals and chemicals).
5. 2,2-methylene (bis-4-methyl-6-tertiary butyl phenol).
6. 2,5-ditertiary butyl hydroquinone.
7. Sterling 12.
8. As hexabromobenzene only.

ELASTOMERIC FLAME RETARDANTS WITH URETHANE

Report Reference No.	Code No.	Urethane		Fluorinated Polymer		Hexabromo-benzene	Halogen[2] Content	Oxygen Index	Viton Formulations
		Spandex	Estane[1]	Viton Cpd	+ Refset				
1.	55-91	—	—		75	25	71.5	100	
2.	57-98			75.75		24.25	60.8	80	Viton 60, Sb_2O_3 6.1, Al_2O_3 6.1, $AlPO_4$ 3
3.	59-104			53.7		46.3	70.8	85	Viton 46.3, PbO 6.94, Diak 0.46[3]
4.	55-94		22.5		18.75	58.75	63	65	
5.	55-93		15		37.5	65.7	65.7	65	
6.	56-97		7.5		37.5	55	72.2	95	
7.	56-95		5.7		45.3	49	72.2	95	
8.	55-92		7.5		56.25	36.25	68.5	75	
9.	53-85		15		50	35	61.4	50	
10.	53-87	7.5			25	67.5	69.75	40	
11.	54-88	5.0			50	45.0	68.4	40	
12.	54-89	2.5			75	22.5	67.25	50	
13.	60-105	4.63		40.9		56.4	68.3	80	Viton 35.1, PbO 5.40, Diak 0.40
14.	61-106	7.5	1.875		9.375	81.25	72.3	50	
15.	61-107	5.0	3.75		18.75	72.5	71.6	50	
16.	61-108	2.5	5.625		28.125	63.75	71.4	75	
17.[4]	55-90		30			70	60	65[4]	
18.[4]	56-96		15			85	73	95[4]	
19.[5]	57-99	11.25				66.75[X]	51.9	45	
20.[6]	57-100	11.25				66.75[X]	51.9	45	

TABLE 15 (Continued)

Report Reference No.	Code No.	Urethane		Fluorinated Polymer		Hexabromo-benzene	Halogen Content	Oxygen Index	Viton Formulations
		Spandex	Estane	Viton Cpd +	Refset				
21.	67-119	5.0		35.0		48.7	68.28	60	MgO,5.25;Diak #1, 0.35; TBPP, 5.70; Viton, 29.4
22.	67-120	5.0		35.0		48.7	68.28		Cu_2O,5.25; Diak #1,0.35; Viton, 29.4; TBPP, 5.70; not cured
23.	68-121	5.0		35.0		48.7	68.28		CuO,5.25; Diak #1,0.35; Viton, 29.4; TBPP, 5.70; not cured
24.	68-122	5.0		35.0		48.7	68.28		FeO,5.25; Diak #1,0.35; Viton, 29.4; TBPP, 5.70; not cured
25.	69-123			43.3		43.3	70.5	60	PbO, 6.5; Diak #1, 0.4; TBPP, 6.5; Physically poor; Viton, 36.4
26.	69-124			43.3		43.3		65	PbO, 6.5; Diak #1, 0.4; Viton, 36.4 Fluorinated oil (Krytox), 6.5; Fluorinated oil bleeds out

1. Estane – 5713
2. Fluorine and Bromine
3. Diak – Curing Agent
4. 30 mil sample
5. Contains Sb_2O_3 14.65%, Al_2O_3 7.35%
6. Contains Decabromobenzene

The urethane-free compounds, however, lack the recovery and elasticity characteristics of Spandex and it is therefore necessary to use urethane in the formulations.

Formulations (Table 15, 4-9) were prepared to show how oxygen index is affected by combining urethane (Estane) with Fluorel. The recovery characteristics of these samples were better than those of the compounds without the urethane; moreover, the samples had high oxygen index values. It is particularly significant that we were able to attain oxygen index values of 95 at halogen contents of 72%, whereas a halogen content of 74 was required when hexabromobenzene was used alone and it was inferior physically.

Estane urethane does not have quite as good recovery characteristics as duPont's Lycra; therefore, once preliminary tests were completed we substituted it for Estane. Compounds containing Lycra with the Fluorel and hexabromobenzene (Table 15, 10-16) have better recovery properties than those containing Estane. Formulation 13, which contains Viton, has an oxygen index of 75 to 80, will burn slowly in 100% oxygen at 4.2 psi and extinguishes in a 70% oxygen/30% nitrogen atmosphere at 6.2 psi. This compound is tough and resilient.

A French patent granted to Raychem Corporation covers the use of a combination of Kynar (polyvinylidene fluoride), antimony oxide, and aluminum phosphate or aluminum oxide with urethanes to make a flame-resistant coating. The theory is that the aluminum causes a more rapid breakdown of the Kynar and thus releases fluorine at a low enough temperature to be an effective flame retardant. We evaluated three formulations (Table 15, 18-20) with Viton, aluminum compounds, and antimony oxide. However, there was no apparent advantage.

Throughout the program we have been seeking a synergistic effect in mixing flame retardants. We had found that copper oxide and hexabromobenzene were synergistic when tested with urethane alone. Therefore, we substituted a number of metal oxides in place of the lead oxide curing agent used with fluorinated elastomers and evaluated them as a supplementary component in formulations containing hexabromobenzene and the fluorocarbon elastomer. However, magnesium oxide, cuprous and cupric oxides, and ferric oxide proved to be ineffective curing agents and yielded soft mushy compounds with unsatisfactory physical properties (Table 15, 21-24).

Table 15, 25 shows the effect of using a reduced level of trisbromochloropropyl phosphate. This flame retardant is not as effective as hexabromobenzene because its halogen content is lower. We also evaluated the use of Krytox, a fluorinated oil, in a formulation containing the fluorinated elastomer and the urethane. The oil is incompatible and bleeds out of the formulation (Table 15, 26).

VI. FIBERS

A. FINAL SELECTION OF FORMULATIONS FOR FIBER SPINNING

Prior to any attempts to spin fibers, we prepared samples to be tested at NASA (Table 16). These formulations were chosen because they had the good physical properties yet extinguished in atmospheres of 35, 70, and 100% oxygen. Samples 1-10 (Table 16) show the relationship between the halogen content and oxygen index as well as the effect of replacing portions of the urethane with fluorinated elastomer. On the basis of NASA's tests, we concluded that:

(1) Sample No. 6, which contains 20% urethane and a combination of hexabromobenzene and trisbromochloropropyl phosphate, has the best combination of properties to meet the 35% oxygen specification. It is advantageous to replace a portion of the urethane with a fluorinated elastomer because the resulting composition has a higher oxygen index value (e.g., Sample 6 vs. Sample 7) and drips less during burning.

(2) Oxygen index values of at least 85 are required to meet NASA's 70% oxygen specification. Formulations 7 and 8 are representative of the systems that best meet the 70% oxygen requirement. These samples have a low concentration of Spandex; the major portion is the fluorinated elastomer. Hexabromobenzene is the major flame retardant in these systems.

(3) Oxygen index values of 95 to 100 are required to meet the 100% oxygen specification. Formulations 13-15 most nearly meet this specification. They burn slowly and finally extinguish. The elastomeric component in these samples is solely the fluorinated elastomer.

B. NASA TEST SAMPLES

Formulations 13-15 (Table 16) were prepared in an attempt to obtain oxygen indexes of 100%. The best of these was Formulation 14. Burning tests at NASA at 100% oxygen showed it burned very slowly and finally extinguished after burning 3 1/4 inches.

In Formulation 72-130 (Table 17) we used the polyurethane synthesized in our laboratory. SA 1138 treated with TDI reacted with a butanediol adipic acid polyester that contained 10% bromine. (See Appendix B; 2b.) It was mixed with hexabromobenzene and trisbromochloropropyl phosphate. The starting material itself has good flame resistance and its oxygen index was about 30. It required less additive to attain an oxygen index of 40-45 and hence reasonably good physical properties were obtained. Formulation 74-132 was a standard formulation containing 20% Spandex and 80% flame retardant-additive. The retardant-additive

TABLE 16

PREFERRED FORMULATIONS

Report Reference No.	Code No.	% Urethane (Spandex)	% Fluorinated Polymer (Viton A)	% Hexabromo benzene	Other Additives	%	% Halogen	Oxygen Index	Comments
1	62-109	40.0		42.0	Trisbromochloro-propyl phosphate	18.0	47.6	35-40	Burned 35 O_2 65 N_2
2	62-110	30.0		49.0	Trisbromochloro-propyl phosphate	21.0	55.5	40.0	Burned 35 O_2 65 N_2 10 psi .02"/sec.
3	63-111	5.0	34.7	48.7	Trisbromochloro-propyl phosphate Lead Dioxide (mono) Diak #1	6.0 5.25 0.35	69.26	76.0	Burned 70 O_2 30 N_2 10 psi S.E. 35 O_2 65 N_2
4	63-112	2.5	34.7	50.45	Trisbromochloro-propyl phosphate Lead Oxide (Mono) Diak #1	6.25 5.25 0.35	71.22	82.0	–
5	64-113	25.0		52.5	Trisbromochloro-propyl phosphate	22.5	61.4	40-45	S.E. 35 O_2 65 N_2
6	64-114	20.0		56.0	Trisbromochloro-propyl phosphate	24.0	63.4	45.0	S.E. 35 O_2 65 N_2
7	65-115	2.5	30.0	62.7	Lead Oxide (Mono) Diak #1	4.5 0.3	74.5	95.0	Slow burning 100% O_2 S.E. 70 O_2
8	65-116	2.5	35.0	56.9	Lead Oxide (Mono) Diak #1	5.25 0.35	72.8	85.0	S.E. 35 O_2 65 N_2 10 psi
9	66-117	2.5	35.0	54.9	Lead Oxide (Mono) Diak #1 Trisbromochloro-propyl phosphate	5.25 0.35 2.00	72.3	83.0	S.E. 35 O_2 65 N_2 10 psi
10	66-118	2.5	30.0	56.0	Lead Oxide (Mono) Diak #1 Trisbromochloro-propyl phosphate	4.5 0.3 6.7	72.7	80.0	–
11	70-125	50			Fluorinated oil (Krytox)	50		Burns in air	Fluorinated oil bleeds out
12	70-126	85			Fluorinated oil (Krytox)	15		Burns in air	Fluorinated oil bleeds out
13	71-127		36.0	58.20	Lead Oxide (Mono) Diak #1	5.4 0.4	73.6	87.0	–
14	71-128		30.0	65.2	Lead Oxide (Mono) Diak #1	4.5 0.3	77.6	100	Burns slowly in 100% O_2 (NASA)
15	72-129		25.0	71.0	Lead Oxide (Mono) Diak #1	3.75 0.25	78.4	100	Physically very poor

TABLE 17

PROPERTIES OF SELECTED COMPOSITIONS

Report Reference No.	Code No.	Flame Retarding Material	ADL Test Data						NASA Test			
			% F.R. in Composition	% Spandex	Halogen in Composition	Oxygen Index	Tensile Strength (psi)	% Elongation	Pressure (psia)	Gas Composition	Propagation Rate (in./sec)	Comments
1	72-130[a]	Hexabromobenzene Tris-1-bromochloro-propyl phosphate	42 18	40%	49.9	45-50	1300	600	10.0	35% O_2 65% N_2	0.16	Good elasticity
2	72-132	Hexabromobenzene Tris-1-bromochloro-propyl phosphate	56 24	20%	62.9	45	880	600	10.0	35% O_2 65% N_2	0.13	Fair elasticity
3	75-133[b]	Fluorinated polymer (Viton A) Hexabromobenzene Tris-1-bromochloro-propyl phosphate	30 45.0 10.2		65.2	55	940	500	10.0 6.2	35% O_2 65% N_2 100% O_2	Self extinguishing 0.5	Poor breaking strength and poor elasticity

a. Polyurethane used for this formulation was synthesized in our laboratory (see Appendix 2B).

b. This formulation also contains 4.5% lead monoxide and 0.3% Diak #1.

was a 7:3 ratio of hexabromobenzene to trisbromochloropropyl phosphate. Formulation 75-133 contains fluorinated polymers; its oxygen index was increased with less halogen but it was somewhat less elastic.

Results obtained from NASA show that Sample 75-133 was self-extinguishing in a 35% oxygen atmosphere at 10 psia, but burned slowly in 100% oxygen at 6.2 psia. Sample 72-130 has good elasticity and burned very slowly in a 35% oxygen atmosphere.

These results indicate that Spandex can be made self-extinguishing in 35, 65, and 100%-oxygen atmospheres with minimum deterioration of physical properties, if a combination of methods developed under this contract are used:

- A synthesized halogenated Spandex (Section IV, Formulation 2A), having an oxygen index of 25 to 30,
- A fluorinated elastomer, plus an organic nonelastomeric flame-retardant additive.

C. FIBER SPINNING

The technique that we used for spinning fibers simulates the procedure that would be used in making duPont Lycra. The spinning dope with flame retardant is pumped through a spinneret with a positive displacement pump and dropped into a water bath to precipitate the fiber and eliminate solvent. The 40 ends next pass through nip rolls which coalesce the fibers and remove excess water. The coalesced fibers pass through a tunnel drier at 80°C to a takeup roll. Figure 8 illustrates the equipment and Figure 9 is a picture of the 40-end spinneret.

The formulation used for our preliminary fiber spinning tests had reasonably good physical properties when tested as a film and passed the NASA 35% oxygen/65% nitrogen flammability test:

Material	Parts by Weight
Spandex	20
Hexabromobenzene	56
Trisbromochloropropyl phosphate in DMF	24

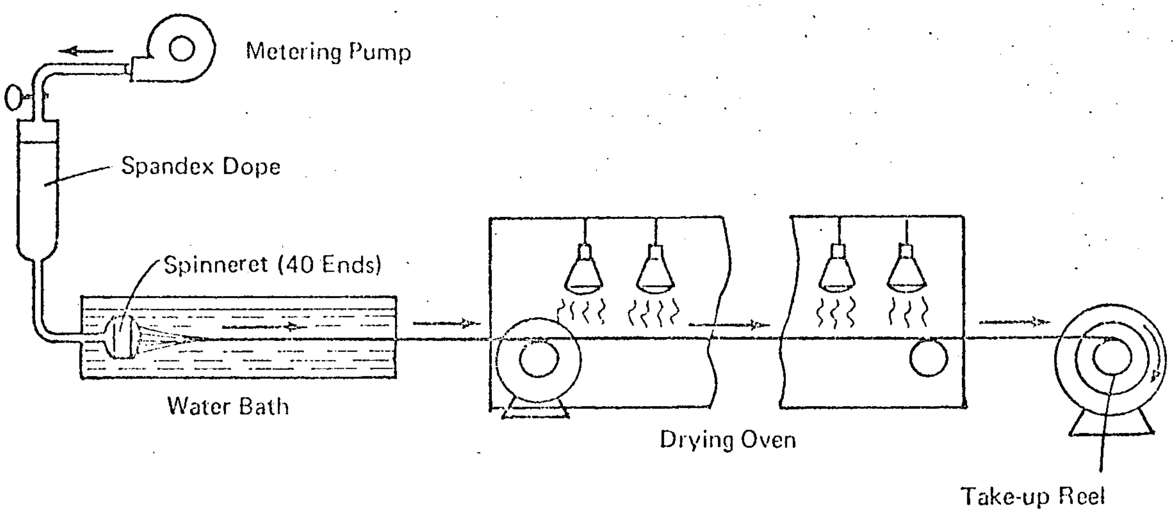


FIGURE 8 SCHEMATIC OF SPANDEX FIBER SPINNING APPARATUS

The ingredients were mixed in a ball mill for 12-16 hours and filtered through cheesecloth prior to use.

We first conducted preliminary tests by forcing the spinning dope through a simple hypodermic needle into a water bath. Fibers were formed and dried in an oven at about 80°C. These had fair properties. Once these preliminary experiments were completed, we used a single-end spinneret to prepare samples of regular Spandex (for control purposes) and some of our formulations. Regular Spandex fibers had excellent properties whereas the modified Spandex had poor physical properties. Scanning electron photomicrographs of cross-sectional views (Figure 10) both show the modified Spandex is porous whereas unmodified Spandex is not. This porosity obviously is responsible for the poor strength.

To reduce individual filament size and eliminate trapped air, we switched over to a 40-end spinneret. The fiber was dropped into the water, run through a series of nip rolls to coalesce fibers and remove excess water, and dried by passing it slowly on a moving belt through a 12-foot drying tunnel which was kept at 80°C by an infrared heater.

Cross-sectional views of this fiber taken with a scanning electron microscope (Figure 11) show a somewhat porous structure, but one vastly better than that obtained with the monofilament. The unmodified Spandex is still less porous and the structure must be improved further, but we believe this improvement can be achieved by modification of the formulation, deaeration and equipment changes.

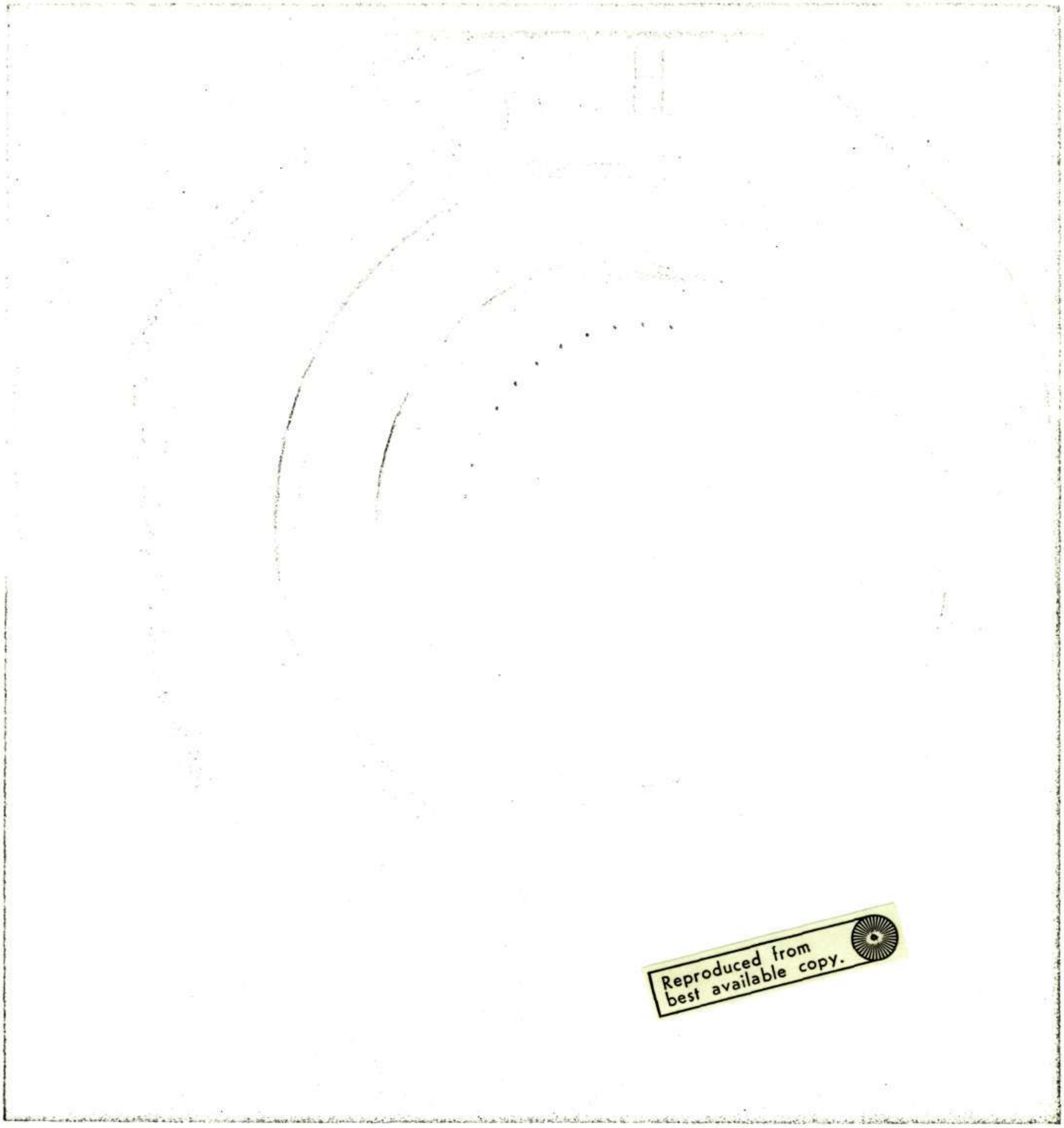
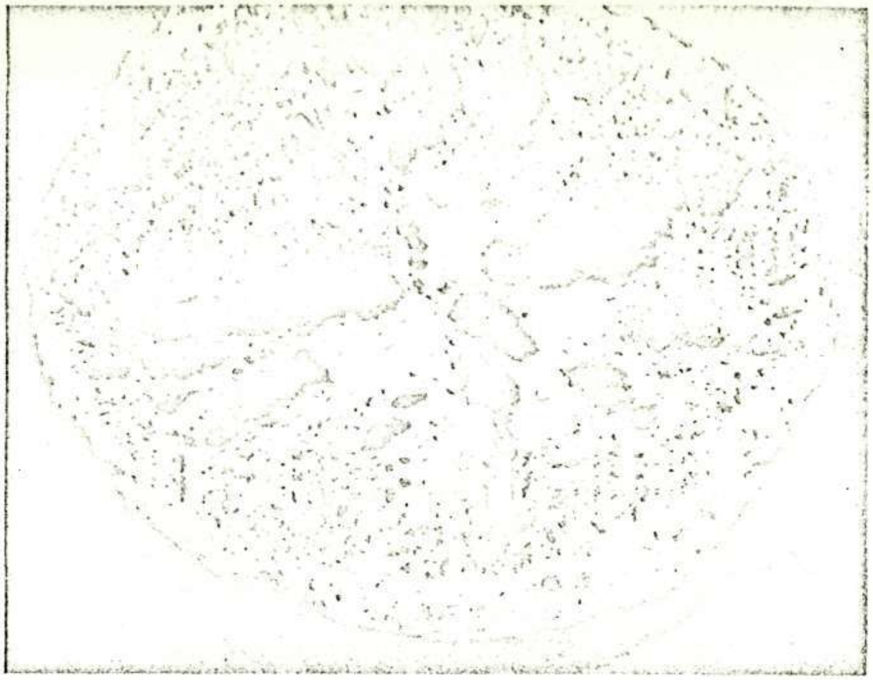
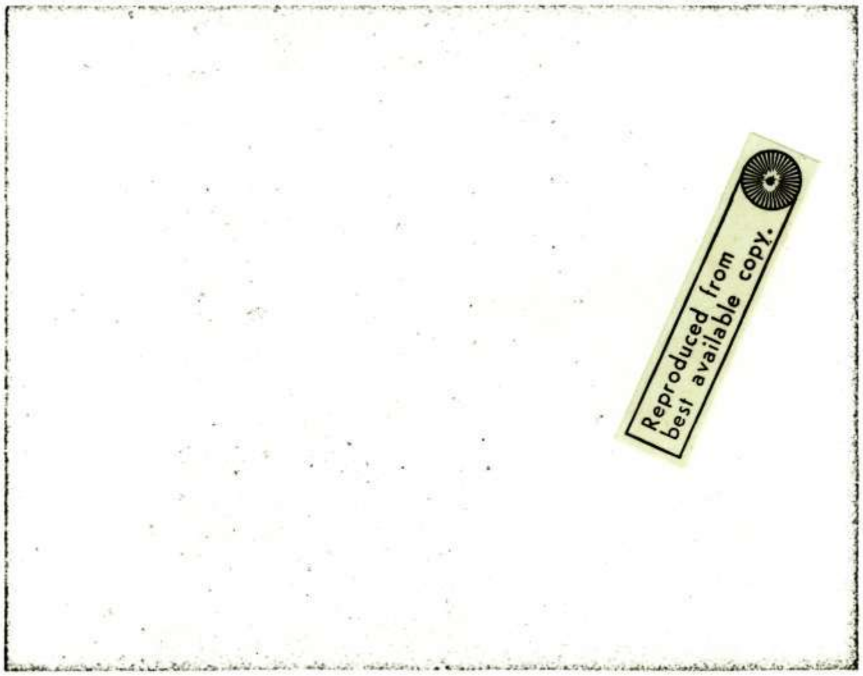


FIGURE 9 FRONT VIEW OF SPINNERET

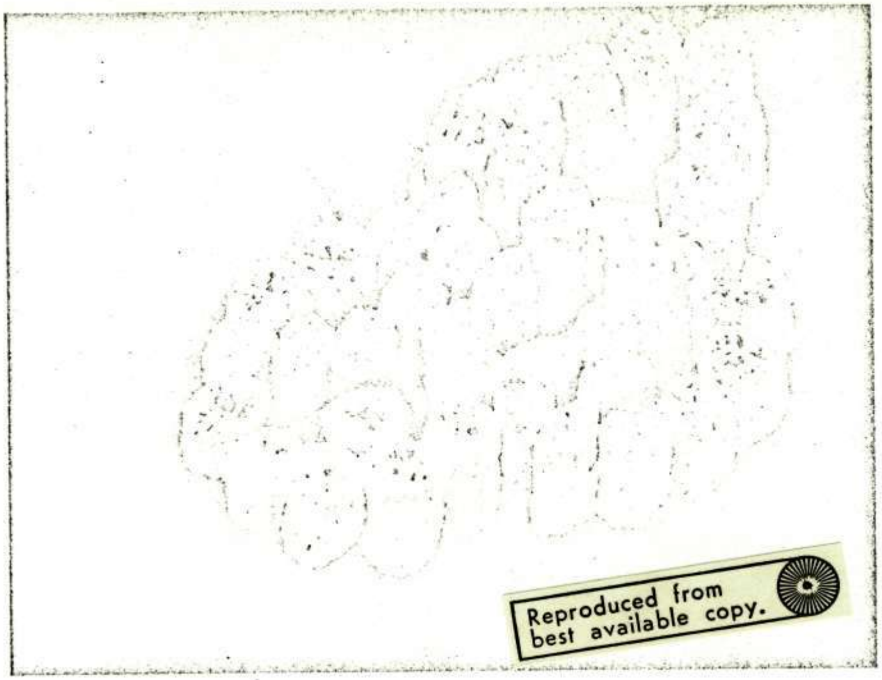


A. Modified Spandex



B. Unmodified Spandex

FIGURE 10 CROSS-SECTIONAL VIEW OF FIBER DRAWN THROUGH A SINGLE-END SPINNERET



A. Modified Spandex

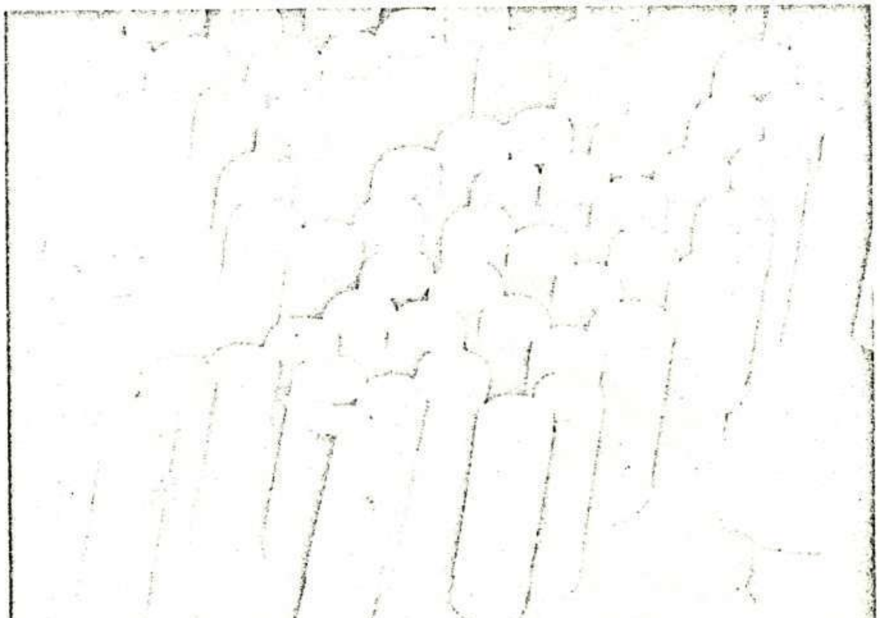


FIGURE 11 CROSS-SECTIONAL VIEW OF FIBER DRAWN THROUGH 40-END SPINNERET

20 C2

VII. CONCLUSIONS

We have synthesized long-chain flexible urethanes that are more flame resistant than any commercially available, and we have also developed flexible urethane compounds with halogenated additives that provide various levels of flame resistance in environments up to 100% oxygen.

To impart the required flame retardancy to Spandex-type urethanes we have had to combine two approaches:

(1) Synthesis of Lycra-type urethanes having halogen atoms in the polymer backbone.

(2) Modification of the synthesized urethanes with flame-retardant additives.

1. Synthesis

A variety of flexible polyurethane structures containing halogen were synthesized from aliphatic or aromatic polyols and dibasic acids. Aliphatic structures could not be used because they are unstable at reaction temperatures. The halogen splits off the chain along with hydrogen and forms hydrogen halide which breaks the ester linkages. Halogen-containing aromatic polyols hold the halogen more tightly and satisfactory products can be made.

The most promising composition was one consisting of a brominated neopentyl glycol capped with toluene diisocyanate, 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 and have an oxygen index value of about 25. They have tensile strength values of about 5,000 psi at 450% elongation.

2. Additives

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-retardant characteristics have been achieved, depending on the levels of additives that are used.

Hexabromobenzene in conjunction with trisbromochloropropyl phosphate (in the ratio 7:3) are effective flame retardant additives for Spandex-type urethane. Hexabromobenzene has a high melting point and good thermal stability. Trisbromochloropropyl phosphate also provides some plasticizing effects to the polymer in addition to imparting flame resistance. The physical properties of the modified polyurethane were directly proportional to the additive present in it and the oxygen index depends on the total halogen in the system. There is a big jump in the oxygen index when the halogen content is increased from 60-80%.

Fluorinated elastomer (Viton) was also found to be an effective additive to other flame retardants in combination with hexabromobenzene and trisbromochloropropyl phosphate. The combination gives better physical properties and flame retardancy at the same halogen content than hexabromobenzene and trisbromochloropropyl phosphate alone.

Cu_2O and SbOCl provide a synergistic effect when used with hexabromobenzene and trisbromochloropropyl phosphate.

3. Fibers

Preliminary work has been carried out on spinning fibers from the compositions we have prepared. Fibers were made using a spinneret with 40 ends.

Further work is required to refine the composition of the elastic elastomeric fibers to achieve maximum strengths on spinning along with maximum flame retardancy. One of the problems is to eliminate a somewhat porous fiber structure which has resulted in low strength. This will best be achieved by changes in both composition and equipment.

VIII. RECOMMENDATIONS

Since the program has shown that urethane Spandex fibers with good flame resistance can be made, we recommend that further work be conducted to refine the techniques that have been developed with the objective of producing fabrics for test. In order to advance this "state of the art" the following steps are recommended:

1. Additional synthesis work should be conducted to increase the molecular weight and purity of the synthesized products. Products such as those obtained by the reaction of PHT 4-diol, hexafluoropentane diol, and dibromoneopentyl glycol should be further modified to increase the halogen content.

2. Additional development should be conducted with additives to achieve synergistic effects, particularly with formulations involving the use of fluorinated polymers, either alone or in combination with the urethanes. This will allow a reduction in additive levels and an improvement in physical properties.

3. Develop optimum techniques for spinning fibers and prepare sufficient materials for the weaving of fabric for test.

4. Much of the information developed under this contract can be useful in improving the flame resistance of other flexible urethane products as well as both rigid and flexible foams. An investigation should be made of these possibilities.

APPENDIX A

MATERIALS USED IN PROGRAM

APPENDIX A

MATERIALS USED IN PROGRAM

Chemicals	Trade Name	Manufacturer
Acetone		Fisher Scientific
Acetic Anhydride		Fisher Scientific
Aluminum Oxide		Fisher Scientific
Aluminum Phosphate		Fisher Scientific
Ammonium Bromide		Fisher Scientific
Ammonium Phosphate		Fisher Scientific
Antimony Oxide	Thermoguard L	Mandt Chemical Co.
Adipic Acid		Celanese Co.
Antimony Trifluoride		Fisher Scientific
Azelaic Acid		Emery Chemicals
	Dechlorane + 25	Hooker Chemical
Bromine		Fisher Scientific
Butanediol		GAF Corporation
Butenediol		GAF Corporation
Carbon Tetrabromide		Aldrich Chemical
Carbon Black	Sterling 12	Cabot Corporation
Chlorobenzene		Fisher Scientific
Chlorinated Diol	HET Acid	Hooker Chemical
Clay	Ultrawhite 90	Minerals & Chemicals
Cobaltic Acetyl Acetonate		
Cuprous Oxide		J. T. Baker Chemicals
Decabromobiphenyl		Michigan Chemicals

APPENDIX A (Continued)

Chemicals	Trade Name	Manufacturer
Dibromo Adipic Acid		Chemicals Labs.
2,3-dibromopropanol		Michigan Chemical
Dibromopentylglycol	SA 1138	Dow Chemical
1,2,3-dibromo-2-butene-1-diol		Aldrich Chemical
Dibutylamine		Fisher Scientific
2,5-ditertiary butylhydroquinone		Eastman Chemical
Dimer Acid	Empel 1010	Emery Chemicals
Dimethylformamide		Fisher Scientific
Ethyl Alcohol		Fisher Scientific
Ferric Oxide		Fisher Scientific
Fluorinated Polymer	Refset	Raybestos-Manhattan Co.
Fluorinated Oil	Krytox	duPont
Halogenated Organophosphorus	RF 272	American Cyanamid
Hexabromobenzene		Michigan Chemical
Hexabromocyclododecane		Aldrich Chemical
Hexachlorobenzene		Eastman Organic Chemical
Hexafluoropentanediol		Peninsula Chemical
Hydrazine		Fisher Scientific
Hydrochloric Acid		Fisher Scientific
Hexamethylene Diamine Carbamate	Diak #1	duPont
Isopropyl Alcohol		Fisher Scientific
1, Karl Fischer Reagent		Fisher Scientific
Lead Oxide		Mallinckrodt Chemical

APPENDIX A (Continued)

Chemicals	Trade Name	Manufacturer
Lithium Bromide		Fisher Scientific
Magnesium Oxide		Fisher Scientific
MDI	Nacconate 300	Allied Chemicals
2,3-methylene (bis-trimethyl-6-tertiary butyl phenyl)		American Cyanamid
Nickel Oxide		Fisher Scientific
Organo Phosphorus	Phosgard C22R	Monsanto
Perfluoroglutaric Acid		Peninsula Chemical
Phthalic Anhydride	PHT 4	Michigan Chemical
Platinum Coated Alumina		Englehard Industries
Polyester	Formeg L8-71	Witco
Polyether	Swift CH 940-321	Swift
Polyether	Swift CH 940-341H	Swift
Polyether	Swift CH 940-371	Swift
Polyvinylchloride		B. F. Goodrich
Polyvinylidenechloride		
Polyvinylfluoride		
Polyvinylidenechloride		Pennsalt Chemical
Potassium Iodide		Fisher Scientific
Silver Nitrate		Fisher Scientific
Sodium Hydroxide		Fisher Scientific
TDI	Naix	Union Carbide
Tetrabromobisphenol A		Great Lakes Chemical
Tetrabromobisphenol S		Great Lakes Chemical

APPENDIX A (Continued)

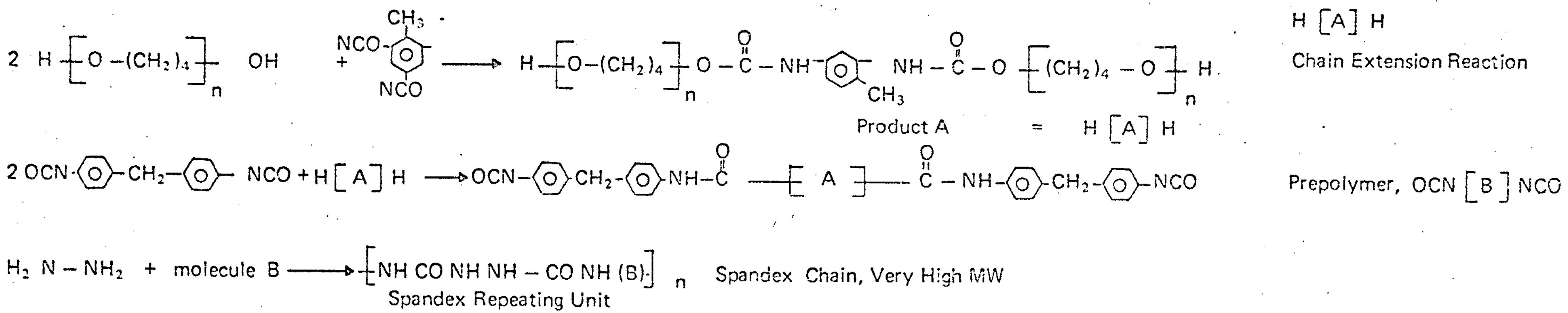
Chemicals	Trade Name	Manufacturer
Tetrabromobutane		Aldrich Chemical
Tetrabromoethane (acetylene tetrabromide)		Michigan Chemical
Tetrabromoethylene Aniline		Michigan Chemical
Tetrafluoroethylene	Treflon	duPont
Tetrahydrofuran		Fisher Scientific
Triphenyl Titanium	Tryer TPT	duPont
Titanium Dioxide		Fisher Scientific
Toluene		Fisher Scientific
Tris-1-bromochloropropyl phosphate	FM 13P	Michigan Chemical
Tris-2,3-dibromopropyl phosphate	FM 23P	Michigan Chemical
Tris-β-chloroethylphosphate	Fryol CEF	Stauffer Chemical
Xylene		
Zinc Borate	Firebrake ZB	U.S. Borax Research
Zinc Oxide		Fisher Scientific

APPENDIX B

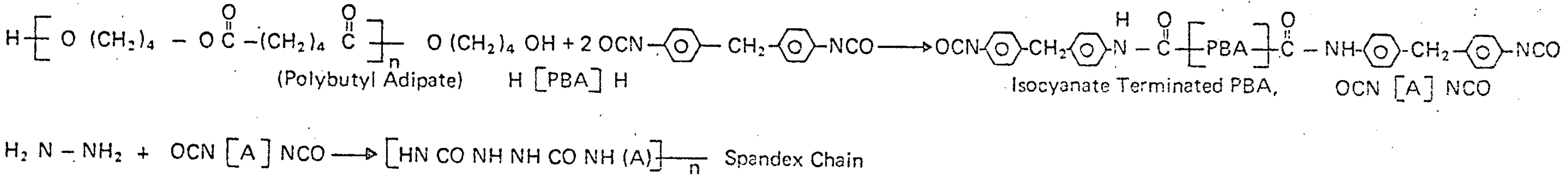
REACTION MECHANISMS

1.0 CONTROL POLYMER SYNTHESIS

A. Polyether Urethane Synthesis



B. Polyester Urethane Synthesis



(1) Polymeg 1000, Quaker Oats, Hydroxy Terminated Polyether

(2) Toluene Diisocyanate, (TDI), Niax Union Carbide, 80% 2, 4 – Isomer, 20% 2, 6 – Isomer

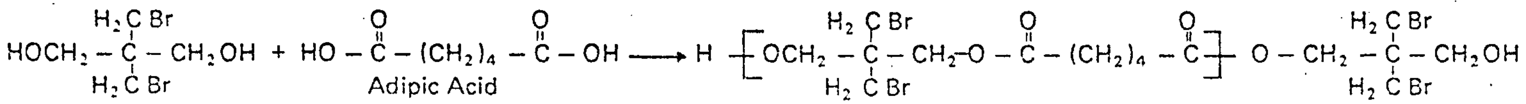
(3) 4, 4′ – Diphenylmethane Diisocyanate, (MDI), Nacconate 300 from Allied Chemical Co.

(4) Polybutyl Adipate, Form Rez L8-71 Witco

(5) Hydrazine, Hummel Chemical

2.0 DOW SA1138 REACTIONS

A. Polyester Synthesis

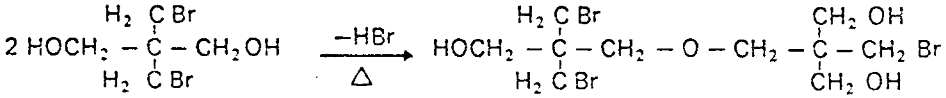


$$HOCH_2-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2OH + \underset{\text{Adipic Acid}}{HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH} \longrightarrow H\left[OCH_2-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]O-CH_2-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2OH$$

SA1138 Adipate

One of the side reactions below prevented the formation of a Spandex type, soluble urethane.

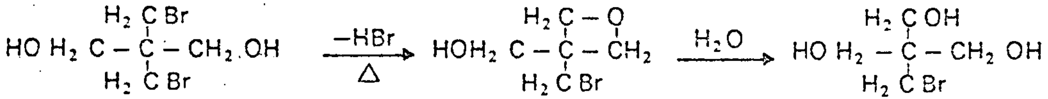
I.



$$2\,HOCH_2-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2OH \xrightarrow[\Delta]{-HBr} HOCH_2-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2-O-CH_2-\overset{CH_2OH}{\underset{CH_2OH}{C}}-CH_2Br$$

Trifunctional

II.

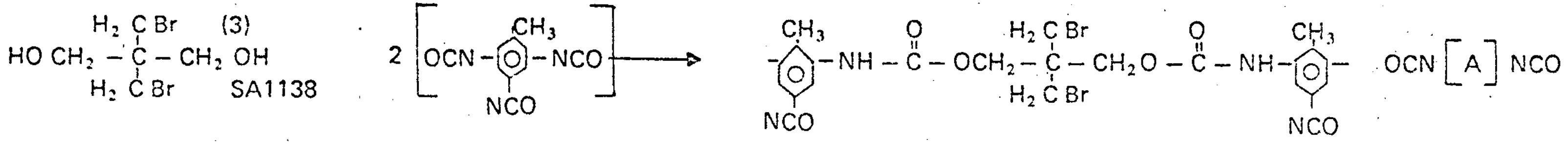


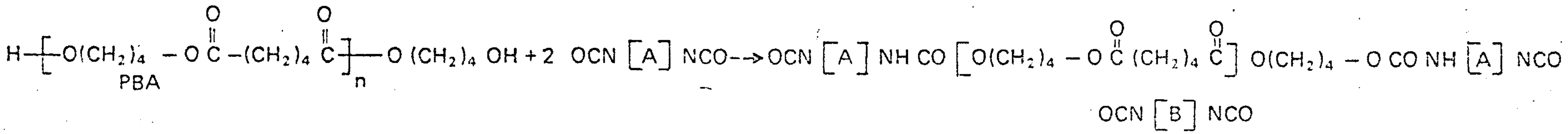
$$HOH_2C-\overset{H_2CBr}{\underset{H_2CBr}{C}}-CH_2OH \xrightarrow[\Delta]{-HBr} HOH_2C-\overset{H_2C-O}{\underset{H_2CBr}{C}}-CH_2 \xrightarrow{H_2O} HOH_2-\overset{H_2COH}{\underset{H_2CBr}{C}}-CH_2OH$$

Trifunctional

2.0 DOW SA1138

B. Use in Prepolymer Preparation





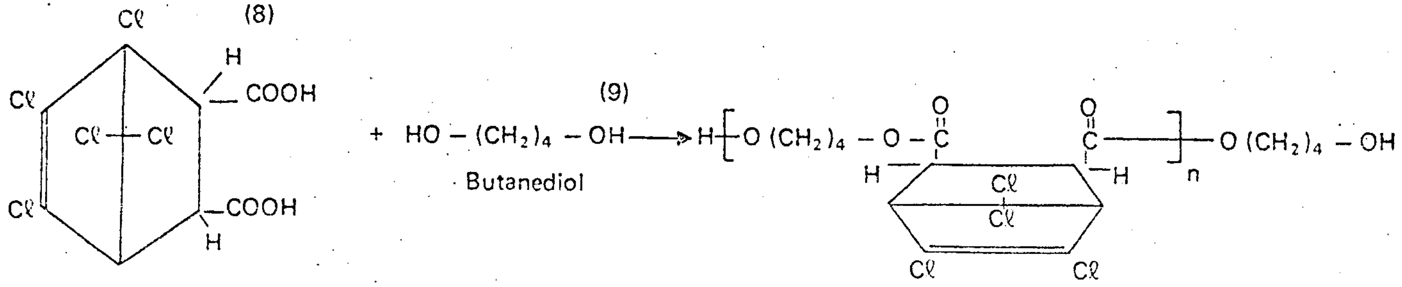
$$H\!-\!\left[O(CH_2)_4-O\overset{\overset{O}{\|}}{C}-(CH_2)_4\overset{\overset{O}{\|}}{C}\right]_n-O(CH_2)_4OH+2\ OCN\boxed{A}NCO\dashrightarrow OCN\boxed{A}NHCO\left[O(CH_2)_4-O\overset{\overset{O}{\|}}{C}(CH_2)_4\overset{\overset{O}{\|}}{C}\right]O(CH_2)_4-OCONH\boxed{A}NCO$$

$$OCN\boxed{B}NCO$$

PBA

$H_2N-NH_2\ +OCN\boxed{B}\ NCO\left[HNCONHNHCONH\,(A)-\right]_n$ Spandex Chain Unit 9.5% Br

3.0 HET ACID



Het Acid

Hydroxy Terminated Polyester

Very Brittle, Not Used

Product too Brittle, Not Used

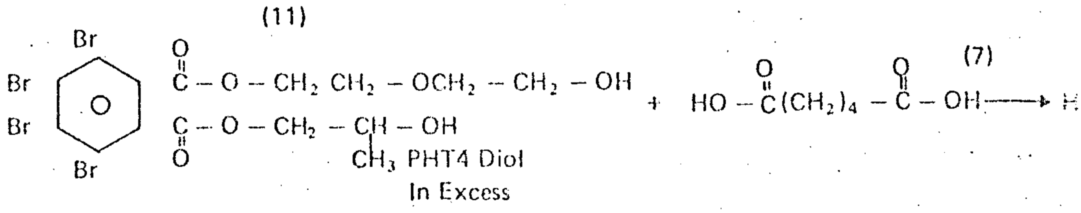
(8) HET Acid, Durez Division, Hooker Chemical

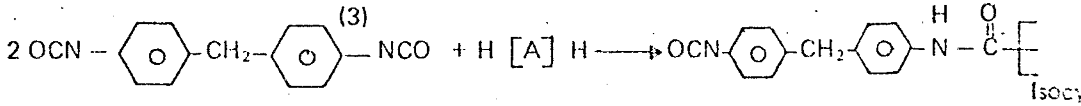
(9) Butandiol, GAF

4.0 PHT4 – DIOL REACTIONS

FOLDOUT FRAME

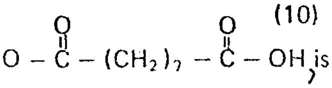
A. Urethane with Adipic Acid





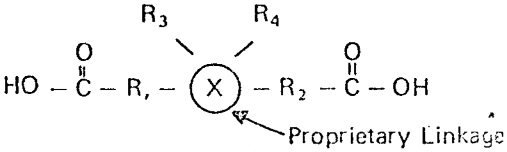
$H_2N-NH_2 + OCN\,[B]\,NCO \left[-NHCONHNHCONH\,(B)-\right]_n$ Spandex Chain

B. Urethane with Azelaic Acid



Same as A above Except Azelaic Acid, $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_7-\overset{O}{\overset{\|}{C}}-OH$ (10), is Substituted for Adipic A

C. Urethane with Dimer Acid



Same as A (and B) above Except Dimer Acid $HO-\overset{O}{\overset{\|}{C}}-R_1-(X)-R_2-\overset{O}{\overset{\|}{C}}-OH$ is S

D. Urethane Using Hexamethylene Diisocyanate in Place of MDI

Same as A except Azelaic Acid was Used Instead of Adipic Acid and $OCN-(CH_2)_6-NCO$ (H

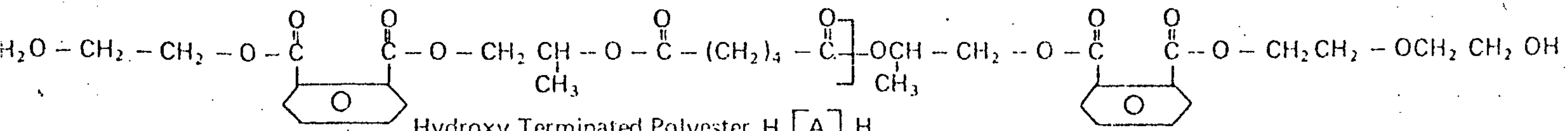
(10) Azelaic Acid, Emery, R_3 and $R_4 \cong 9C$, R_1 and $R_2 \cong 8C$

(11) PHT4 Diol, Firemaster from Michigan Chemical

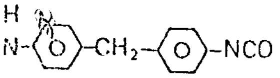
(12) Hexamethylene Diisocyanate Mobay HX

FOLDOUT FRAME 2

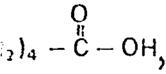
PRECEDING PAGE BLANK NOT FILMED



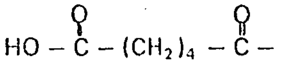
Hydroxy Terminated Polyester, H [A] H



d Polyester Prepolymer, OCN [B] NCO



$_2)_4 - \overset{O}{\overset{\|}{C}} - OH$, in the 1st Reaction; the Polyester Reaction

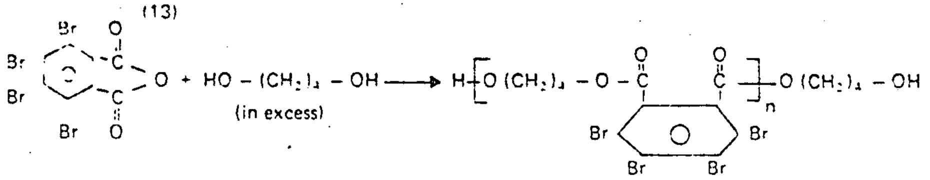


pic Acid $HO - \overset{O}{\overset{\|}{C}} - (CH_2)_4 - \overset{O}{\overset{\|}{C}} - OH$ in the 1st Reaction; the Polyester Reaction.

f MDI (3)

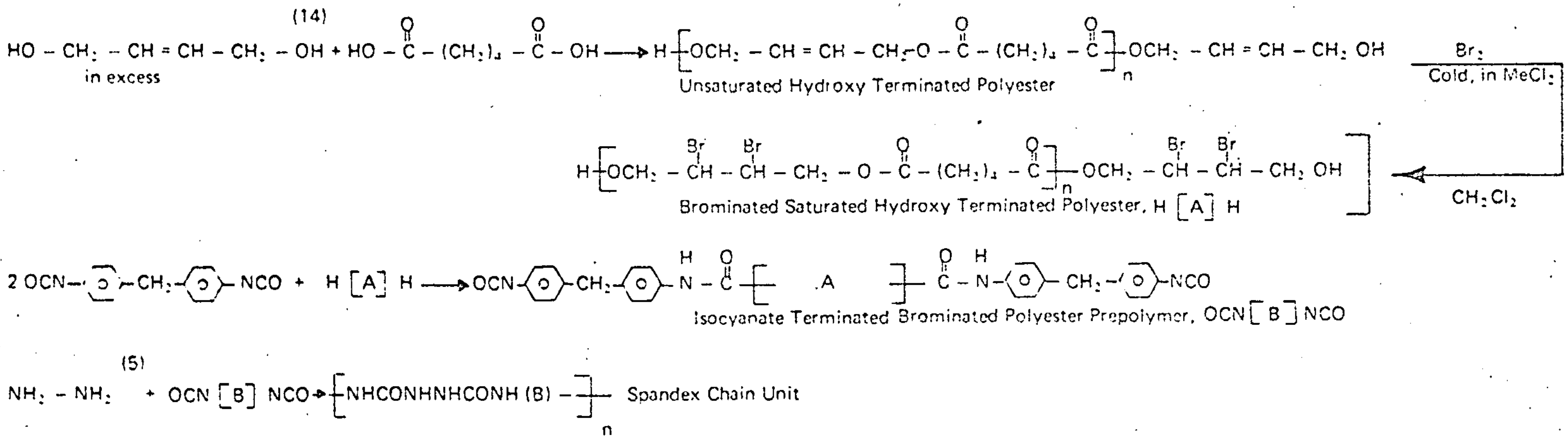
13

5.0 PHT4 POLYESTER WITH BUTANEDIOL

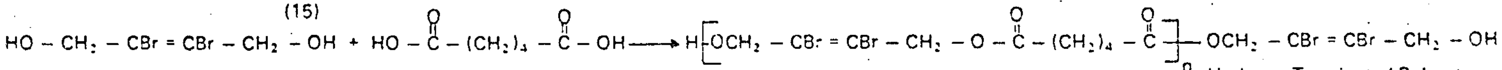


Hydroxy Terminated Polyester
Not Used Because of HBr Evolution
and Degradation

6.0 POST BROMINATION OF A BUTENEDIOL – ADIPIC ACID POLYESTER



7.0 TRANS – 2, 3, – DIBROMO – 2 – BUTENE – 1, 4, – DIOL – ADIPIC ACID POLYESTER

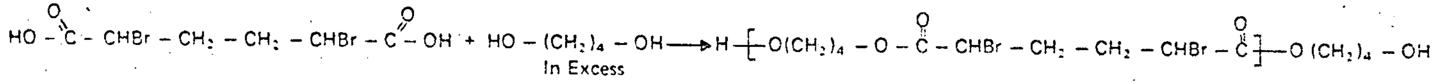


$$HO-CH_2-CBr=CBr-CH_2-OH + HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \longrightarrow H\left[OCH_2-CBr=CBr-CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OCH_2-CBr=CBr-CH_2-OH$$

Hydroxy Terminated Polyester
Not Used Due to HBr Evolution
and Degradation

(13) Tetrabromophthalic Anhydride, Michigan Chemical
(14) Butenediol, GAF
(15) Aldrich Chemical Co., No. 14, 370-7, Samp. No. 011281

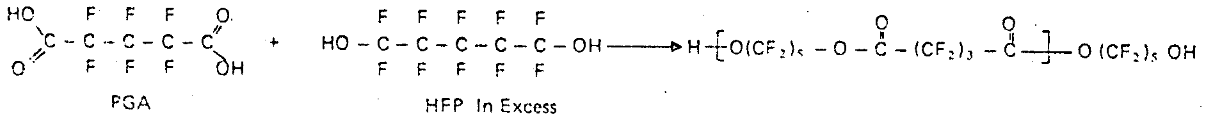
8.0 DIBROMOADIPIC ACID – BUTANEDIOL POLYESTER



$HO-\overset{O}{C}-CHBr-CH_2-CH_2-CHBr-\overset{O}{C}-OH + \underset{\text{In Excess}}{HO-(CH_2)_4-OH} \longrightarrow H\left[O(CH_2)_4-O-\overset{O}{C}-CHBr-CH_2-CH_2-CHBr-\overset{O}{C}\right]O(CH_2)_4-OH$

No Product Recovered
Hydroxy-Terminated Polyester
Not Used, Degraded

9.0 PERFLUOROGLUTARIC ACID – 2, 2, 3, 3, 4, 4 – HEXAFLUORO – 1, 5 – PENTANEDIOL



$\underset{\text{PGA}}{HOOC-CF_2-CF_2-CF_2-COOH} + \underset{\text{HFP In Excess}}{HO-CF_2-CF_2-CF_2-CF_2-CF_2-OH} \longrightarrow H\left[O(CF_2)_5-O-\overset{O}{C}-(CF_2)_3-\overset{O}{C}\right]O(CF_2)_5OH$

No Product Recovered
Degraded

10.0 SWIFT POLYMERS

C 4940-321 C 4940-341 C4940-371	Polyethers with Br and P	Used 1.0 A and 1.0 B Type Reactions, No Useful Product Obtained

(16) Chemicals Procurement Laboratories Inc., College Point, New York

(17) Perfluoroglutaric Acid, Peninsular Chemresearch Inc., 01-13-270-44

(13) Hexafluoropentanediol, Peninsular Chemresearch Inc., 01-16320-09

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Report, 1 Jan. 1970 - 1 Jan. 1971 J.T. Unclas
Howarth, et al (Little (Arthur D.), Inc.)
CSCL 11E G3/18 35794
Mar. 1971 87 p

FFNo 672 Aug 65