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DEVELOPMENT OF NONFLAMMABLE ADHESIVES

Alfred H. McLeod
Walter P. Fitzgerald, Jr.
of

Whittaker Corporation
Research & Development Division
San Diego, California

FINAL TECHNICAL REPORT

January 1970

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FOREWORD

This report was prepared by Whittaker Corporation, Research and Development Division, under Contract No. NAS9-8428, entitled "Development of Nonflammable Adhesives," for the Manned Spacecraft Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Crew Systems Division, with Dale Sauers acting as Project Officer. The research work was conducted in Whittaker's R&D laboratory by Floyd D. Trischler, Senior Chemist and Alfred H. McLeod, Chemist, who served as program managers and principal investigators. Also contributing to the program were Edward S. Harrison, Chemist and Harlan Wooster, William Warner and James Charter, Senior Laboratory Technicians. This report covers the period from 17 September 1968 to 20 January 1970.

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ABSTRACT

Fluorinated polyurethanes based on the polyether of perfluoropropylene oxide and 1-chloro-3,5,6-trifluoro-m-phenylene diisocyanate were examined as nonflammable adhesives. Additives were investigated as a potential route to improved nonflammable properties. Certain modifications of these fluorinated polyurethanes resulted in a broad temperature range adhesive system with improved elevated temperature performance and acceptable nonflammable properties. Block polymers were prepared from the fluorinated polyurethanes which, when tackified, resulted in an unusual pressure sensitive adhesive. Scale-up studies were conducted on the materials used on this program.

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INTRODUCTION AND OBJECTIVES

A critical need for materials which do not support combustion was found for use in the spacecraft environment as a result of the fire aboard the Apollo Spacecraft. The oxygen atmosphere complicates the problem, since materials which are nonflammable in air become highly flammable under the pure oxygen conditions found in the spacecraft. The main objective of this program was the development of a broad temperature range adhesive system which would not support combustion, and could consequently be used throughout the temperature range of -320°F to $+530^{\circ}\text{F}$. The second purpose was to develop a pressure sensitive adhesive which also would not support combustion in oxygen.

For NASA use, Whittaker Corporation, Research and Development Division pioneered the development of LOX-compatible adhesives⁽¹⁾ based on highly fluorinated polyurethanes. These materials were found to be rapidly self-extinguishing in an oxygen atmosphere. Because of other desirable properties, such as excellent adhesion, room temperature cure, and good strength properties, the fluorinated polyurethanes were selected as the material most likely to fulfill the objectives of this program.

(1) The Development of Structural Adhesive Systems Suitable for Use With Liquid Oxygen, Summary Report V, Contract NAS8-11068, Dec 1967.

SUMMARY

General purpose nonflammable adhesives based on Polymer I are unsatisfactory for our purposes due to poor elevated temperature strength. In addition, the incorporation of additives to this system offers no improvement in nonflammability properties.

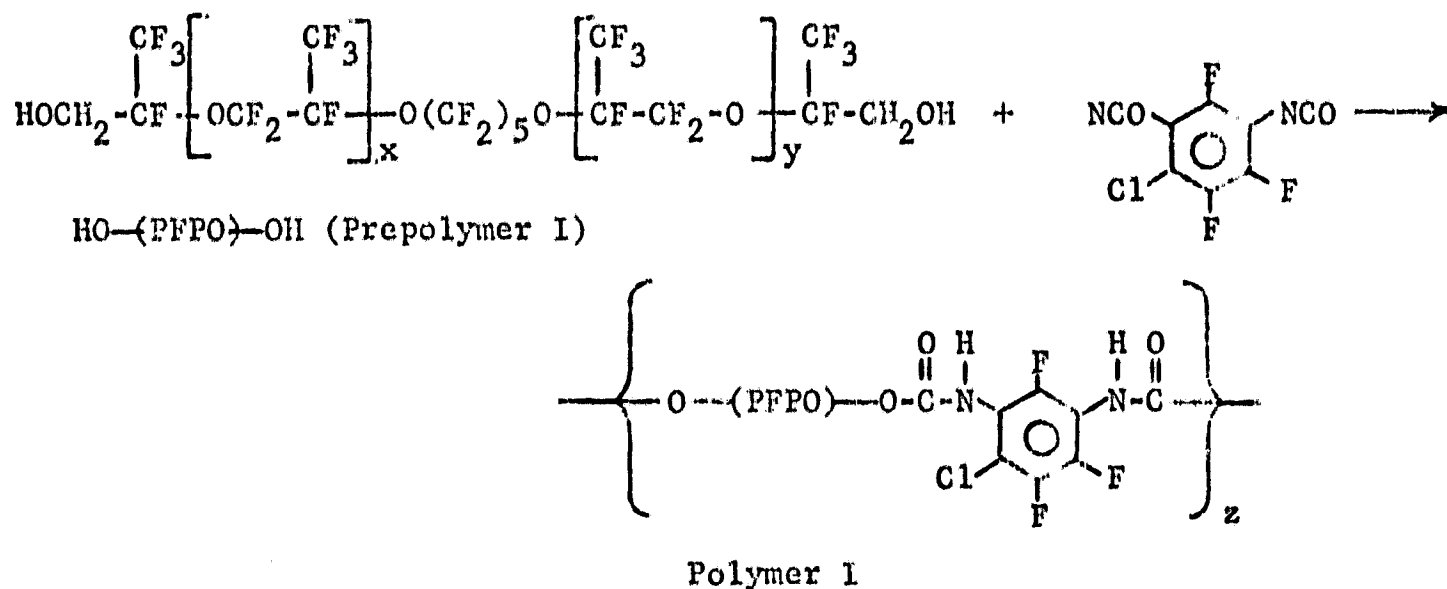
A general purpose adhesive was prepared from highly fluorinated polyurethanes with segmented blocks found to improve elevated temperature properties. The modified polymer, coded Polymer A, had acceptable nonflammability properties in addition to elevated temperature properties superior to the Polymer I system.

The linear fluorinated polyurethane system was found to be unacceptable as the base resin for the pressure sensitive adhesive. A segmented polyurethane-polycarbonate was prepared which, when tackified, resulted in an acceptable pressure sensitive adhesive.

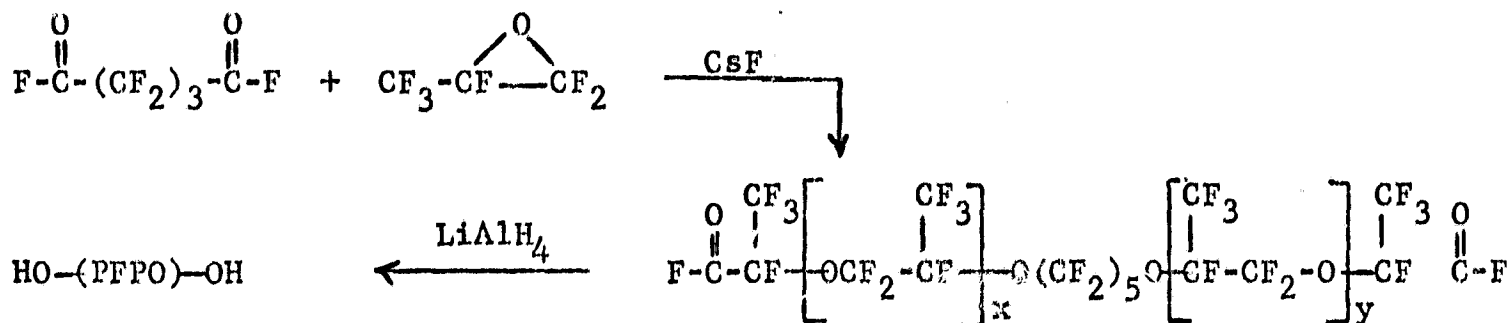
DISCUSSION

BROAD TEMPERATURE RANGE ADHESIVE

The fluorinated polyurethanes have been prepared from the hydroxyl-terminated polyether of perfluoropropylene oxide by extension with fluorinated diisocyanates in the following manner:



The required fluorinated polyether is prepared as follows:



Only very limited flammability data had been obtained previously on this fluorinated polyurethane. These data indicated that it was rapidly self-extinguishing in a 16.5 psi 100% oxygen atmosphere. The objective of the program, however, was to render the material nonflammable under these conditions. In order to improve the nonflammability of this fluorinated polyurethane, a number of fireproofing additives were investigated. Slab stock of the polymers containing additives was prepared and submitted to NASA-Houston for flammability testing in accordance with MSC-A-D-66-3-A. The results of this testing are listed in Table I. Photographs of some of the materials which were subjected to the flammability test are presented in Figures 1 and 2. While the basic polyurethane was self-extinguishing at 16.5 psi in a 60% oxygen-40% nitrogen atmosphere, only Cab-O-Sil and asbestos were found to be effective in rendering the

TABLE I

EVALUATION OF FIREPROOFING ADDITIVES IN THE FLUORINATED POLYURETHANE ADHESIVE

FLAMMABILITY TEST RESULTS (PER MSC-A-D-66-3-A, BOTTOM IGNITION)						
Sample No.	Fire Proofing Additive	16.5 psi-60% O ₂ /40% N ₂				6.2 psi-100% O ₂
		Tissue Ignitor	1" x 0.22" Silicone Ignitor	Tissue Ignitor	1" x 0.22" Silicone Ignitor	1" x 0.22" Silicone Ignitor
2129-11A	None (control)	SE (6)	--	SE (6)	B (0.156)	PLN-2338
2129-13J	5 phr-Sb ₂ O ₃	SE	B (0.357)	SE	--	PLN-2347
2128-8	25 phr-Sb ₂ O ₃	SE	--	SE	B (0.50)	PLN-2224
2128-9	67 phr-Sb ₂ O ₃	SE	(1)	(1)	(1)	PLN-2223
2129-3	25 phr-Asbestos	NF	--	B (0.142)	--	PLN-2221
2129-5	25 phr-TiO ₂	SE	--	SE	B (0.833)	PLN-2215
2129-6	6 phr-Cab-O-Sil	NF	--	SE	--	PLN-2216
2129-7	5 phr-Alon C (2)	SE	--	SE	B (0.312)	PLN-2217
2129-11C	7 phr-Alon C (2)	SE	--	SE	--	PLN-2341
2129-11B	10 phr-Alon C (2)	SE	--	SE	B (0.125)	PLN-2340
2129-12E	20 phr-Al ₂ O ₃ (2)	SE	--	SE	B (0.227)	PLN-2343
2129-12G	10 phr-Eymal (2)	B (0.833)	--	--	--	PLN-2345
2129-8	25 phr-FR 28 (3)	B (0.66)	--	--	--	PLN-2218
2129-9	25 phr-Syn. Mica	SE	--	SE	B (0.66)	PLN-2219
2129-12D	20 phr-Eccosphere (4)	SE	--	SE	B (0.208)	PLN-2342
2129-12F	60 phr-Cu Powder	SE	--	SE	B (0.27)	PLN-2344
2129-13H	20 phr-ZnO	SE	--	SE	B (0.313)	PLN-2346
0120-78 (5)	None	SE (6)	--	SE (6)	B (0.227)	PLN-2338

NF = Nonflammable

SE = Self-extinguishing

B = turns with burn rates in inches/second

phr = parts per hundred resin

(1) Insufficient sample for additional testing

(2) Aluminum oxide

(3) Inorganic borate

(4) Silica microballoons

(5) Polymer A

(6) Identical results obtained when the polymer was tested on β-glass

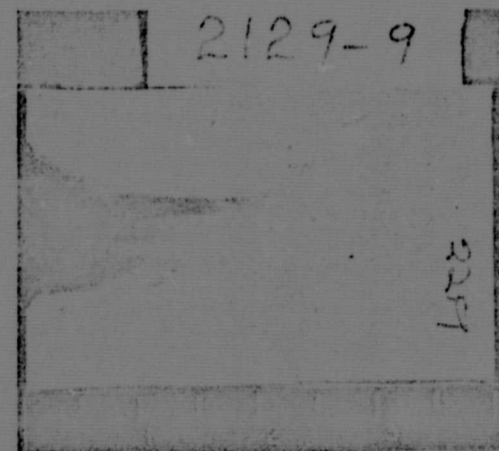
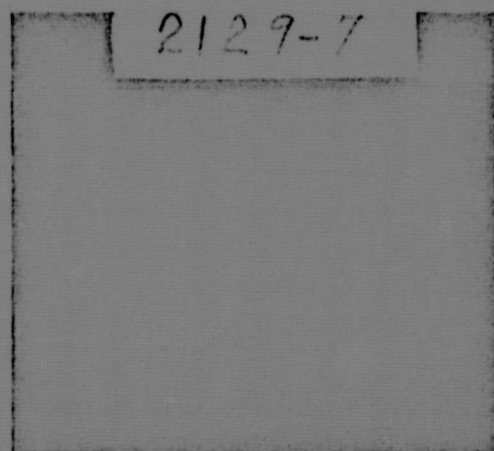
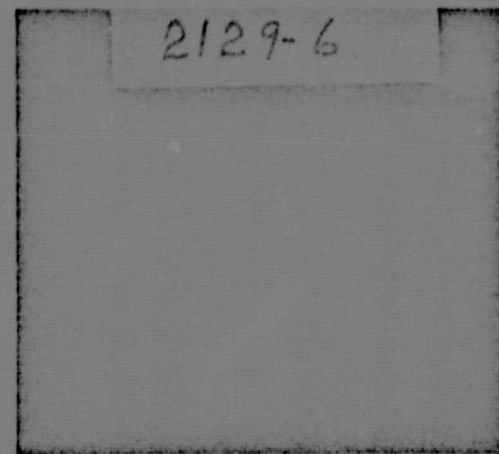
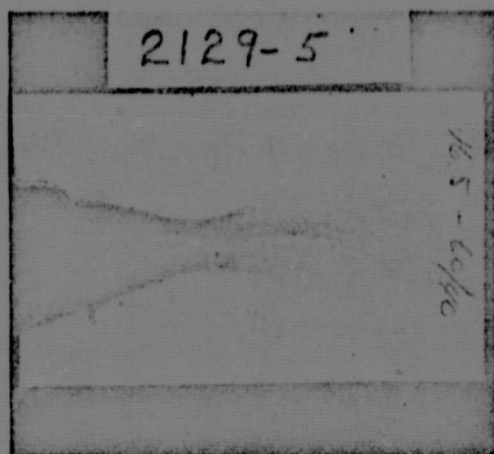
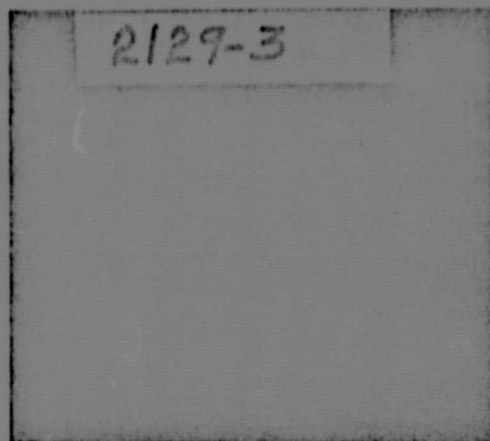
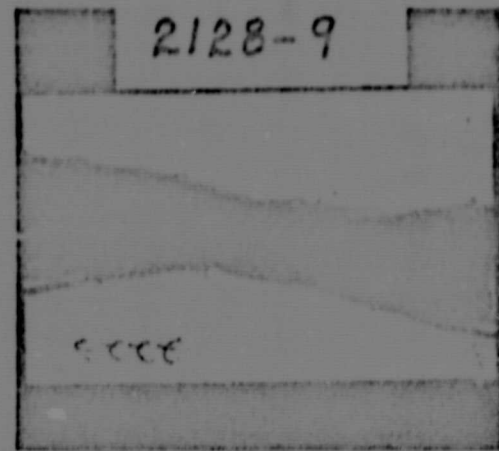
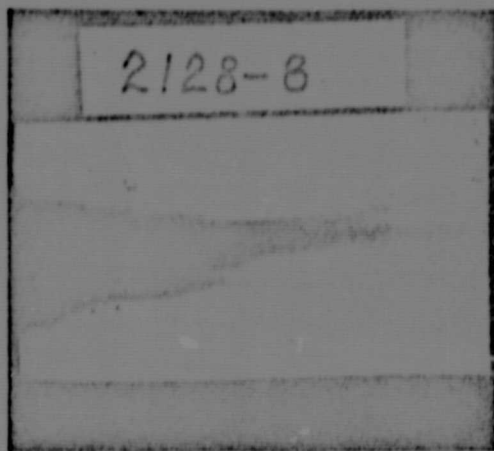


Figure 1. Test Specimens after Flammability Testing at 16.5 psi, 60% Oxygen - 40% Nitrogen (Tissue Paper Ignitor)

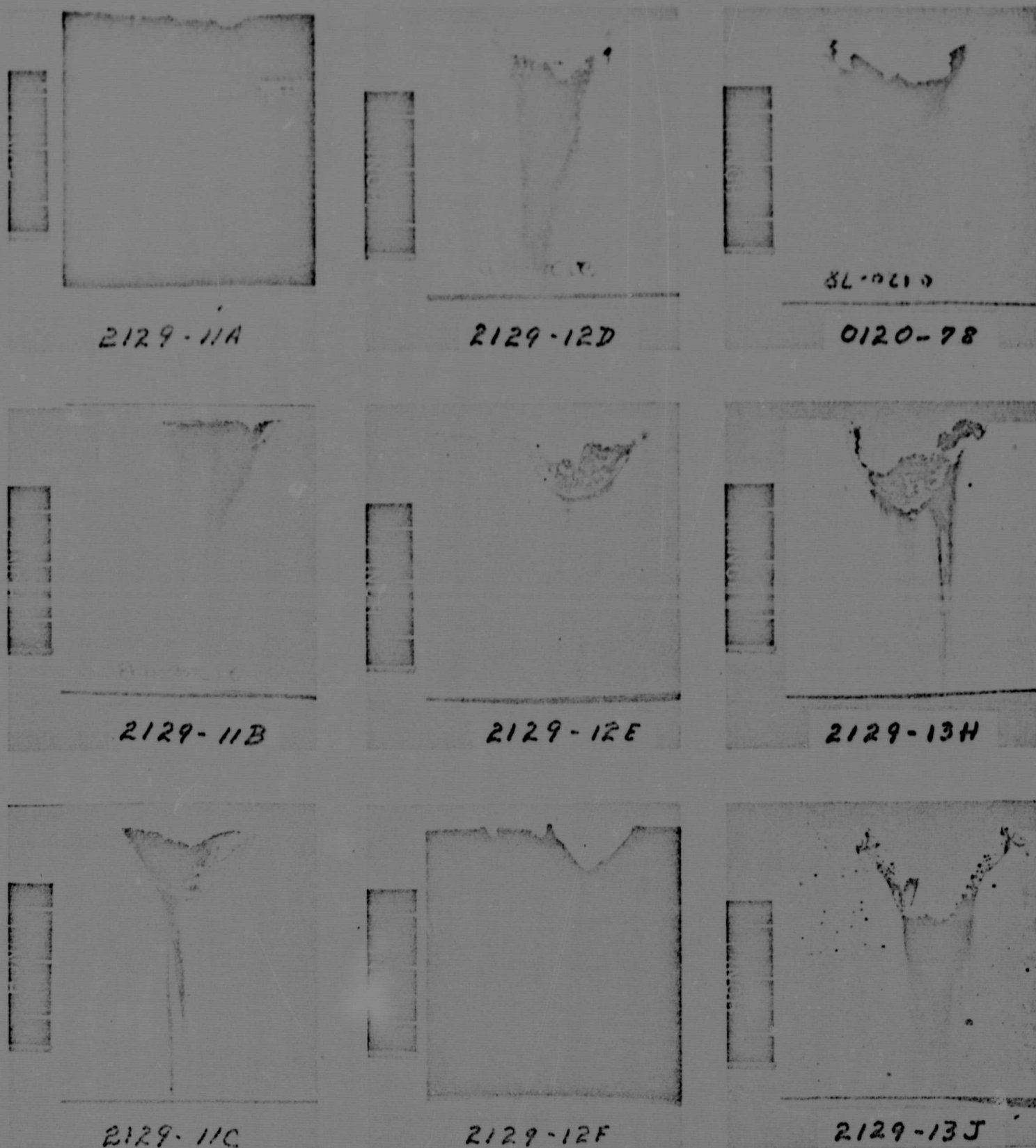


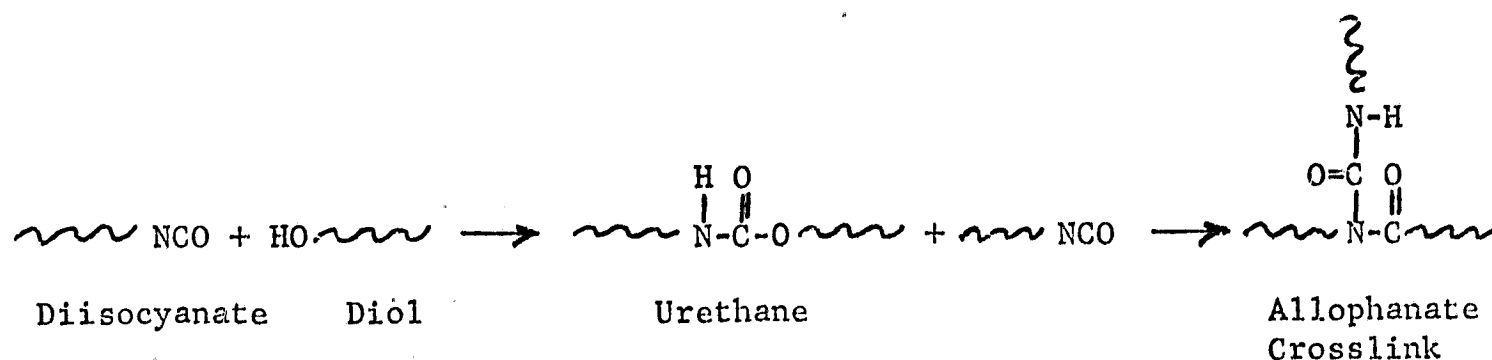
Figure 2. Test Specimens after Flammability Testing at 16.5 psi,
60% Oxygen-40% Nitrogen (Tissue Paper Ignitor)

product nonflammable. Several additives, such as Bymal (aluminum oxide) and FR-28 (inorganic borate), actually resulted in a product which burned. In no case was the polymer nonflammable in the 16.5 psi 100% oxygen environment.

Subsequent to the award of the contract, the spacecraft environment was altered to provide two less severe conditions, namely: (1) 16.5 psi, 60% oxygen/40% nitrogen at launch and (2) 6.2 psi, 100% oxygen during orbit.* Furthermore, the flammability requirements were eased somewhat in that the product would satisfy MSC's flammability requirements* if the adhesive were self-extinguishing under the above conditions. In addition, it was specified that the future development effort should be directed toward improving the other physical properties of the adhesive system within the flammability requirements specified above.* Based on the results in Table I and Figures 1 and 2, there appeared to be no obvious flammability problem with the fluorinated polyurethane.

Consequently, the temperature-strength profile of this polymer was determined in order to establish the useful range of the material as a structural adhesive. The results are depicted in Figure 3. As the test data indicate, this material demonstrated excellent low temperature properties, probably attributable to the rotational freedom donated by the fluorinated ether groups in the polyether. Once the temperature was raised above 150°F, however, the strength declined drastically, again probably due to the increased mobility of the same polyether segments at elevated temperatures.

Up to this point, the fluorinated polyurethanes had been cured (crosslinked) by using excess diisocyanate, which reacts with the urethane groups to form allophanate crosslinks.



Allophanate crosslinks are typically weak at elevated temperatures, and this results in poor bond strengths above +200°F. Nevertheless, this adhesive has excellent properties over the range of -320°F to +150°F.

* Letter, Mr. R. E. Smylie to F. D. Trischler, dated 15 November 1968.

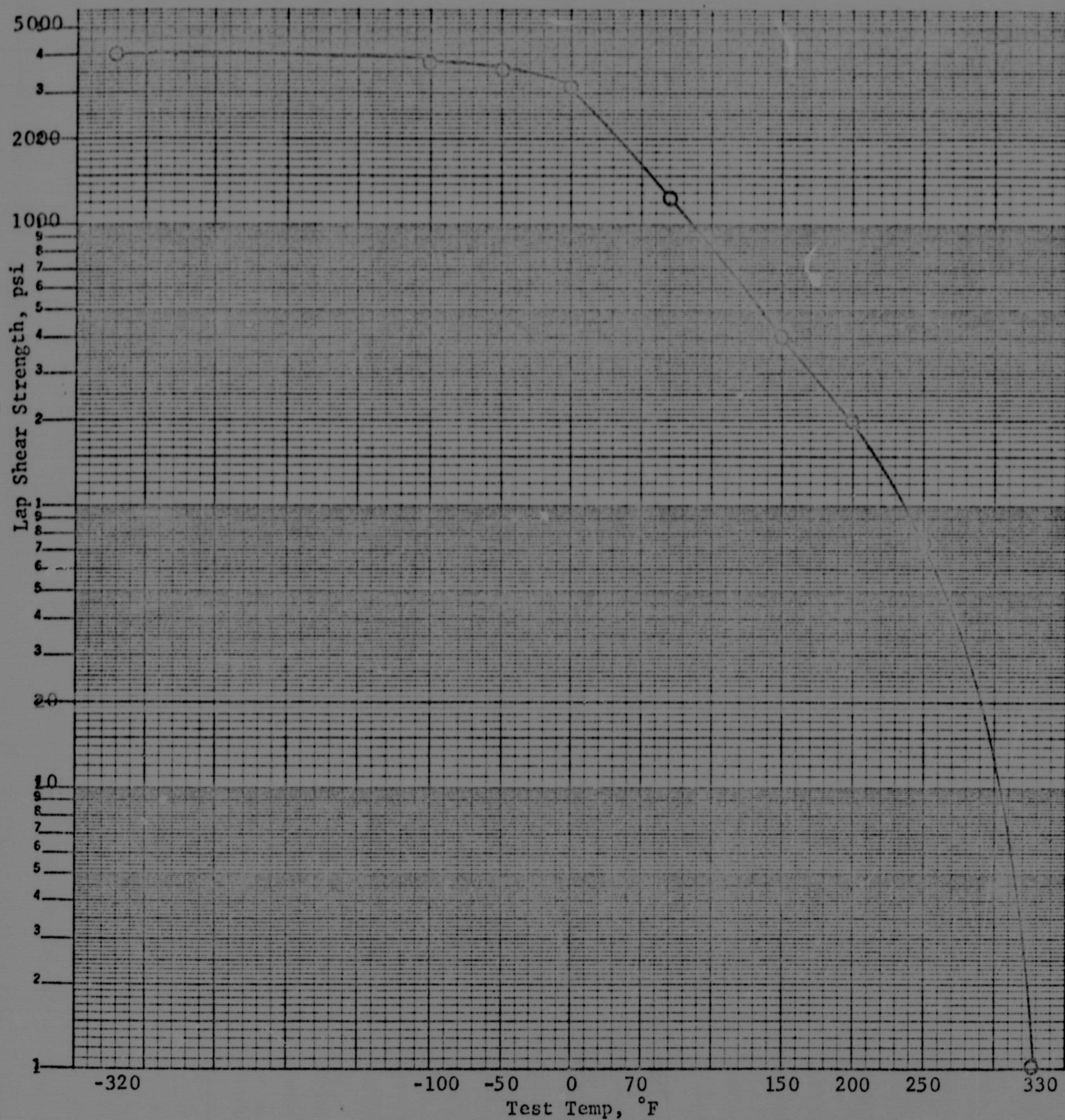
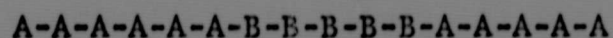


Figure 3. Temperature-Strength Profile of the Fluorinated Polyurethane Adhesive

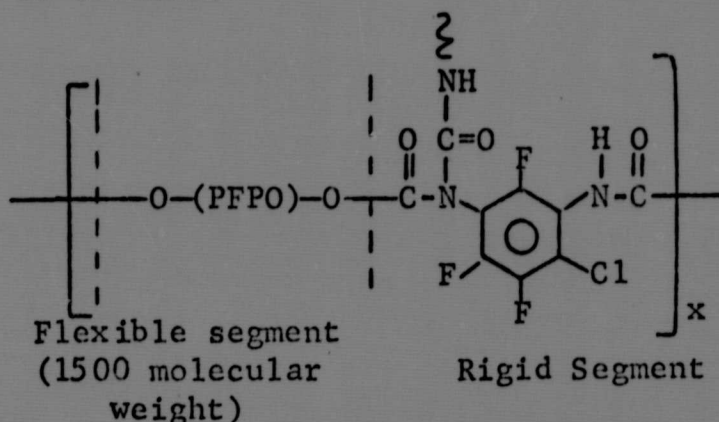
Since the unmodified polyurethane system was unacceptable as an adhesive for use at temperatures up to the required +330°F, suitable block extension was required to improve thermal capability.

One type of polymer exhibiting high temperature properties contain bulky aromatic groups. Increased rigidity, with a concomitant increase in physical properties, may also be achieved by incorporating highly polar groups such as amides, ureas and esters into the polymer chain. Therefore, a logical scheme for improving the elevated temperature performance of the fluorinated polyurethane is to re-design the system to incorporate bulky aromatic groups, preferably containing highly polar groups, into the polymer chain. This alteration can most conveniently be achieved by preparing a block polymer. For example, a polymer having the required components could be represented as follows:

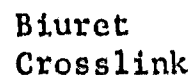


If "A" represented the flexible molecular segment of the polymer chain, these groups would have a high degree of molecular mobility at low temperature and would consequently impart low temperature physical properties to the system. The "B" portion of the polymer represents the rigid segment, imparting the elevated temperature physical properties to the system. It must be understood, however, that this type of system should exhibit reduced low temperature properties as compared with an entirely flexible polymeric material, along with lower elevated temperature performance than an all-aromatic material. Nevertheless, this type of system should have good overall physical properties over the broad temperature range required.

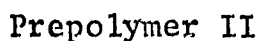
In the present fluorinated polyurethane, the polymer chain may be represented as follows:



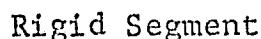
In addition to incorporating bulky groups into the polymer backbone, thermally stable crosslinks are required in order to retain elevated temperature performance. A feasible route to achieving this objective is to utilize an amine cure mechanism to form urea linkages. Excess diisocyanate can then react with the urea groups to form biuret crosslinks.



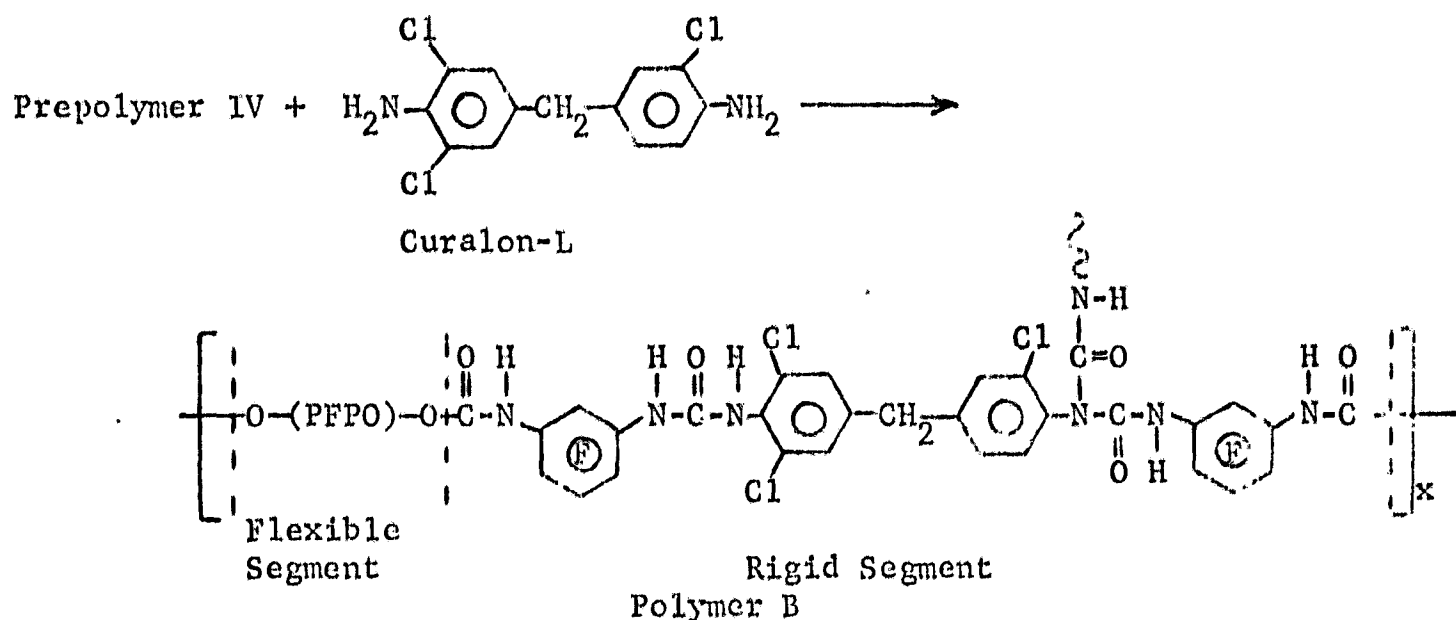
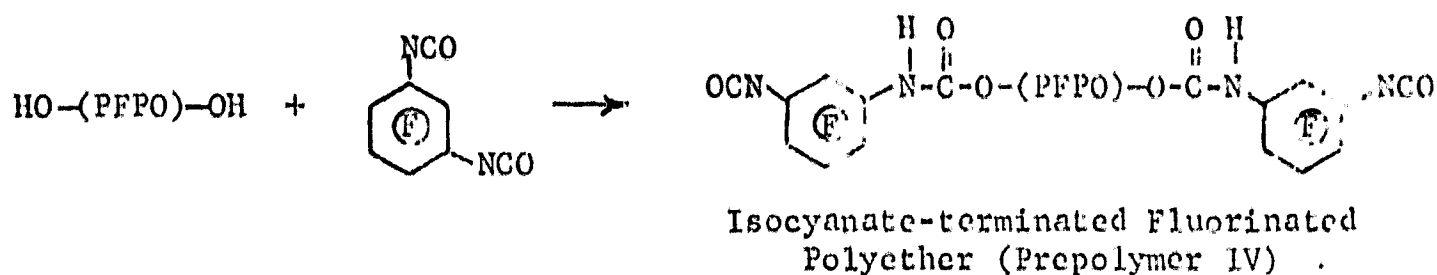
In order to evaluate a biuret-crosslinked polyurethane, an isocyanate-terminated prepolymer was prepared from the polyether of perfluoropropylene oxide as follows.



Prepolymer II + 



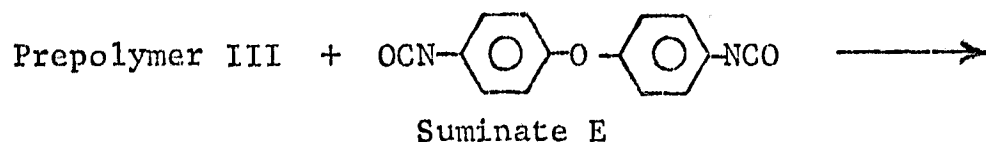
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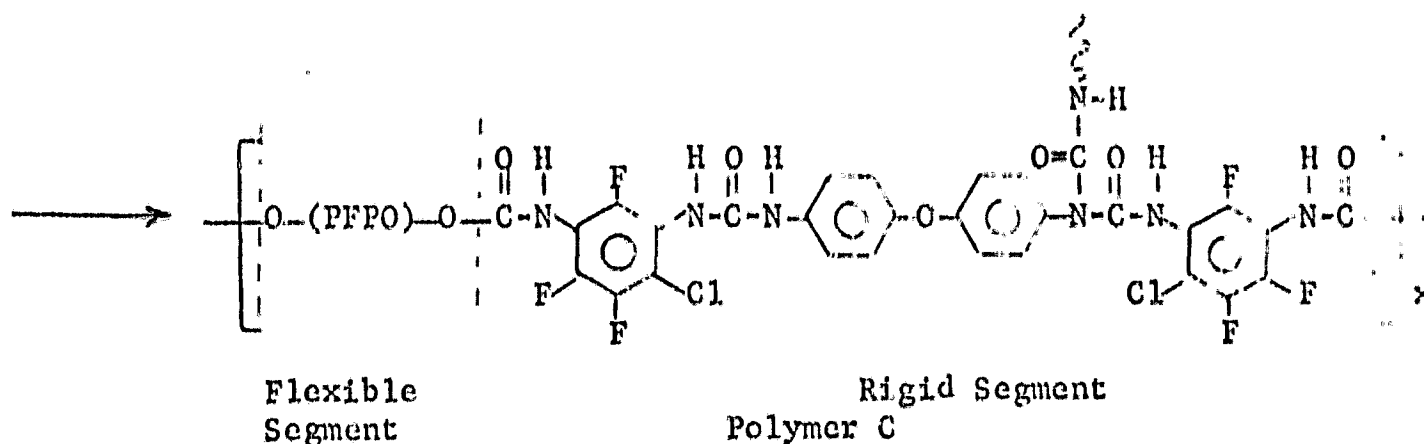


This polymer was a tough elastomer at temperatures up to 350°F. It was more rigid at room temperature than the original polyurethane investigated on this program. In addition, it was self-extinguishing in oxygen in our preliminary flammability test in ca. 100% O₂.

While Polymer B has excellent properties, the reaction of Curalon L with Prepolymer IV proved to be so rapid that it was unacceptable as an adhesive.

An alternative method was devised which resulted in a polymer (Polymer C) having properties very similar to Polymer B, and whose reactivity was attenuated sufficiently to permit its evaluation as an adhesive composition. Polymer C was prepared from Prepolymer III and "Suminate E" as follows:





Polymer C was evaluated as an adhesive system and the results are summarized in Table II.

TABLE II
EVALUATION OF POLYMER C AS A
BROAD TEMPERATURE RANGE ADHESIVE SYSTEM*

Set No.	% Suminate E	Postcure	Tensile Shear Strength, psi		
			-320°F	RT	+200°F
Original Fluorinated Polyurethane			4200	1200	170
13A	7.1	--	250	1105	294
13B	8.5	--	168	640	248
13CA	14.2	--	144	635	428
13CB	14.2	Overnight at 200°F	89	1480	620
13CC	14.2	8 hr at 250°F	653	2410	1109
13CD	14.2	4 hr at 300°F	459	1729	649

* All specimens were cured overnight at RT, followed by 2 days at 160°F.

As shown in the above table, Polymer C demonstrated potential as an elevated temperature adhesive if a postcure of 8 hours at 250°F was used. Furthermore, a sample of polymer from Set 13A was found to be self-extinguishing at 16.5 psi 60% oxygen/40% nitrogen when applied to β -glass (Test Sample No. 2129-21A).

Since Polymer Set 13CC displayed excellent properties at +200°F, a temperature-strength profile of this material was determined which is shown in Figure 4. This polymer displayed good adhesive properties up

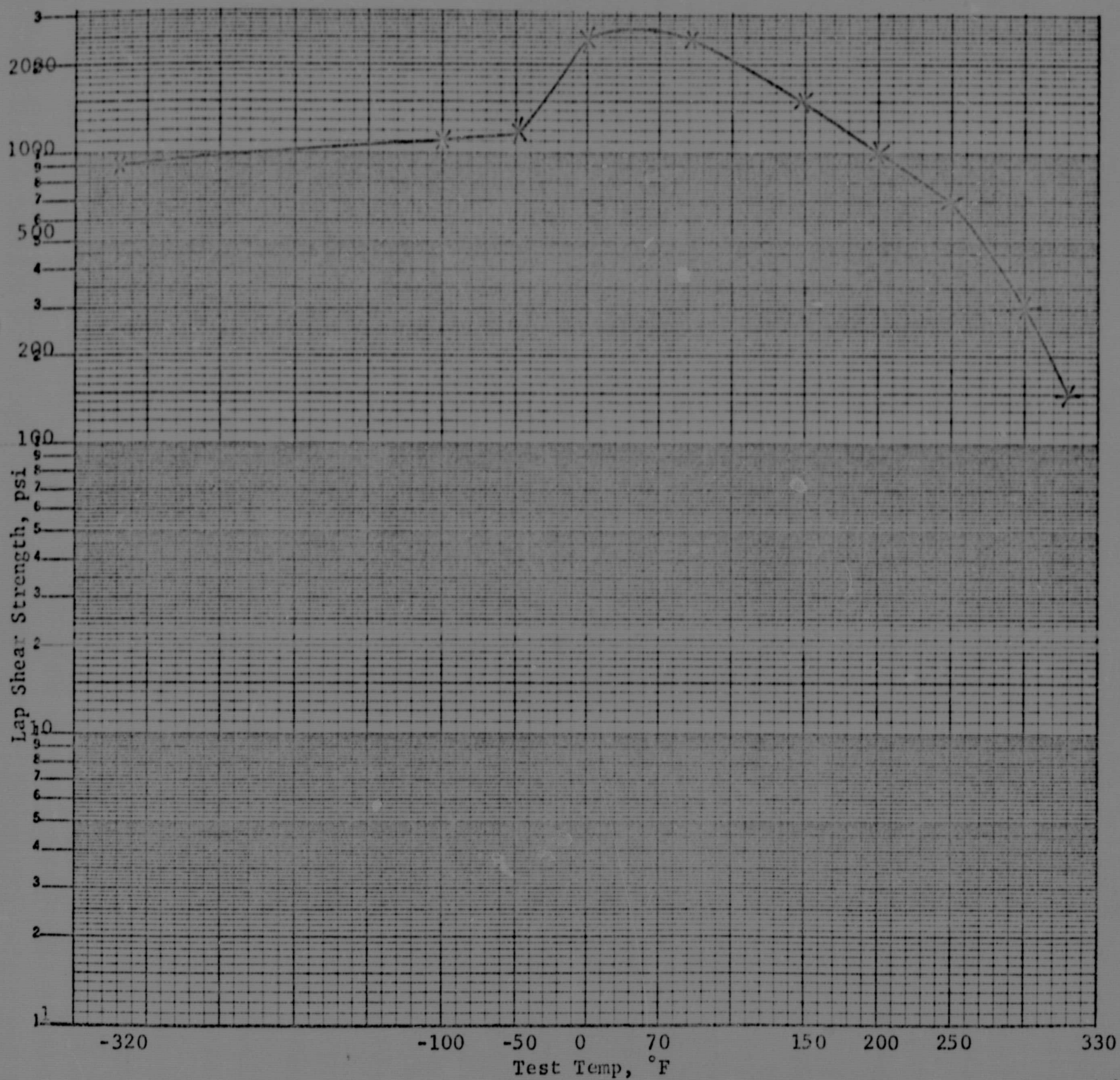
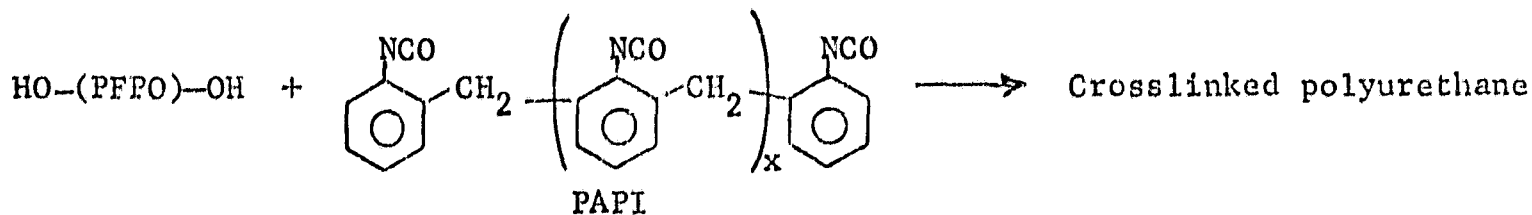
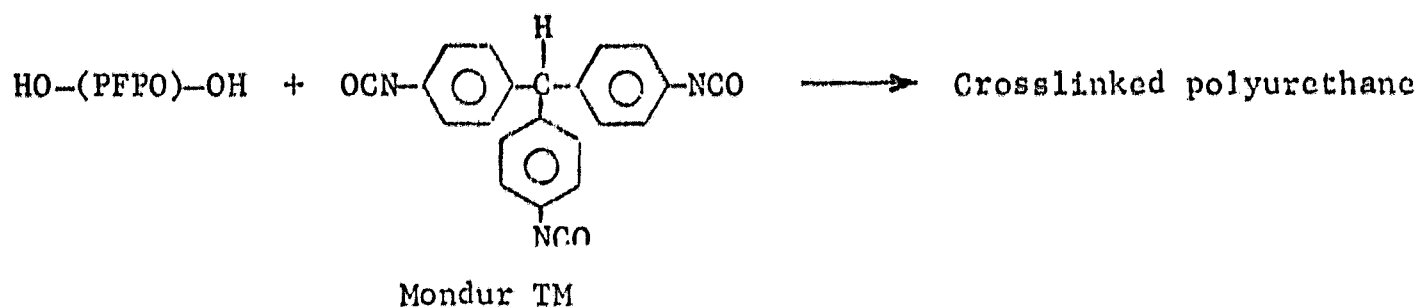


Figure 4. Temperature-Strength Profile of the Polymer C Adhesive (from Set 13CC)

to +330°F. Unfortunately, it was found to be flammable, probably due to the higher concentration of hydrogen-bearing Suminate E required (Test Sample No. 2123-24).

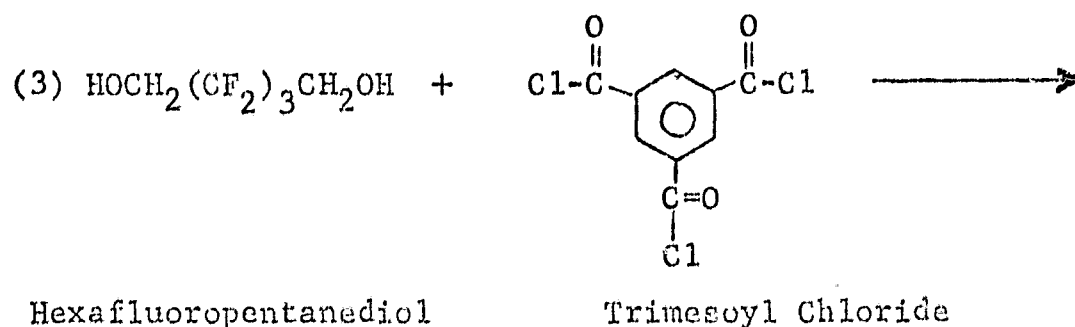
A modification of Polymer C was also prepared, which contained one-half of the required stoichiometric amount of diisocyanate as Suminate E and the other half as 1-chloro-3,5,6-trifluoro-m-phenylene diisocyanate. While this polymer also burned (Test Sample No. 2129-27B), in 16.5 psi 60% O₂:40% N₂, the burn rate was 50 percent of the original Polymer C. It is believed possible that a further modified Polymer C can be made which has the required elevated temperature properties while retaining the necessary nonflammability characteristics, but lack of time and funding prevented the execution of this study.

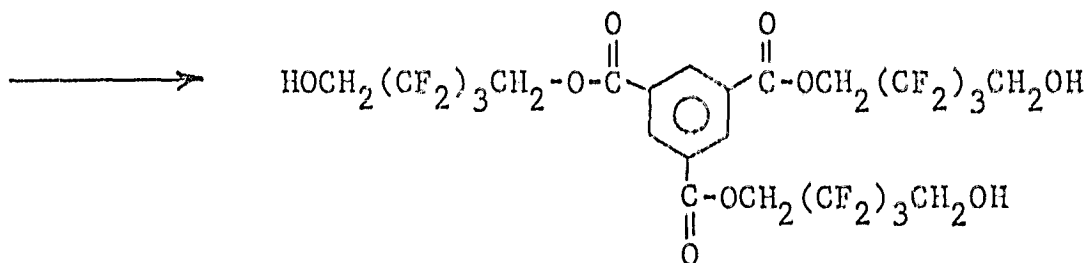
An alternate method of improving the high temperature strength of the fluorinated polyurethane utilized a trifunctional crosslinking reaction. Two commercially available polyisocyanates (Mondur TM and PAPI) were screened as potential curing agents for the polyether of perfluoropropylene oxide.



Unfortunately, neither of the polyisocyanates were soluble in the polyether and failed to react at a reasonable rate.

A trifunctional crosslinking agent (Crosslinking Agent X) was prepared from trimesoyl chloride and hexafluoropentanediol as follows:

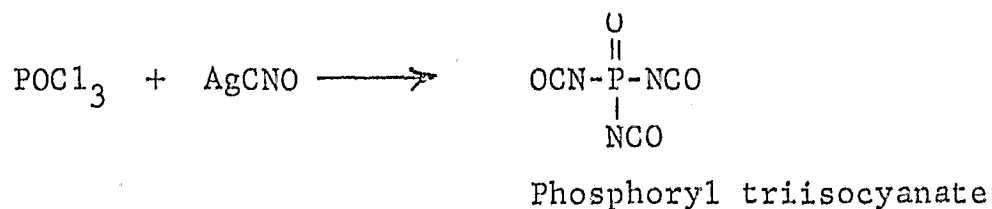
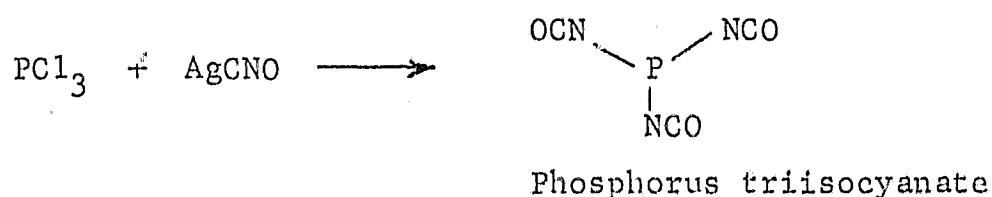




Crosslinking Agent X

The adhesive which was prepared by reacting crosslinking Agent X with Prepolymer II was, however, found to have inadequate strength at the elevated temperatures. In addition, the polymer burned under the required test conditions (Test Sample No. 2129-27A).

Two alternative, potentially useful crosslinking agents, phosphorus triisocyanate and phosphoryl triisocyanate, have been reported which were hoped might dramatically improve the requisite properties of the fluorinated polyurethane. These compounds have been prepared as follows.



These materials have been widely investigated to make fire-retardant polyurethanes from commercially available starting materials. Consequently, it was hoped that incorporation of a portion of such a tri-functional material would result in urethane crosslinks in our perfluorinated system which should impart improved elevated temperature performance to the cured adhesive and improve nonflammability characteristics.

Attempts made to prepare phosphorus triisocyanate in our laboratory using silver cyanate and phosphorus trichloride were unsuccessful. The preparative technique reported in the literature only listed a 10% yield of products. A recent article, however, reported a procedure for preparing the same compound in 60% yield by using sodium cyanate. Due to the short duration of the program, and monetary limitations, this route could not be pursued further.

Various other trifunctional curing agents for this system were also studied at WRD under a separate contract.* These curing agents were based primarily on extension through melamine and melamine-terminated prepolymers. While it was found that improved properties could be obtained by incorporation of the melamine, the systems were not processable. They were, however, rapidly self-extinguishing at 6.5 psi O₂ with tissue ignitor (NASA-MSO test).

Polymer A was the most promising polymeric system which retained acceptable nonflammability properties on β -glass (Sample 2129-27C). While the temperature-strength properties were inadequate, it was believed that a higher temperature cure might improve this situation. Consequently, an adhesive was prepared from Polymer A which was cured overnight at 160°F, followed by 8 hours postcure at 250°F. Based on the promising results in Table III, Polymer A has intermediate elevated temperature properties between the flammable Polymer C and the original polyurethane. This nevertheless represents a distinct improvement.

TABLE III
EVALUATION OF POLYMER A ADHESIVE SYSTEM

Test Temp, °F	Tensile Strength, psi			
	Polymer A Tin Catalyst	Polymer A Iron Catalyst	Polymer C	Original Polyurethane
-320	3120	350	900	4190
RT	3670	1020	2450	1150
+200	532	580	950	170
+300	--	150	300	0
+330	24	50	140	0

An additional improvement was made by lowering the catalyst concentration from 0.1% iron to 0.005% tin. The initial change from an iron to a tin catalyst was necessitated by the iron catalyst imparting a residual "linseed oil" odor to the adhesive which was considered objectionable. The lower concentration of stannous octoate catalyst also greatly reduced the possibility of the catalyst bleeding out with time, eventually causing a flammability problem.

* Contract NAS8-24389, "The Development of Structural Adhesive Systems for Use With Liquid Oxygen".

It is firmly believed that a further improved adhesive system based on Polymer A can ultimately be developed, since important variables such as stoichiometry, molecular weight, cure cycle, catalysts, and additives have not been fully studied under current funding. Work on the permanent bonding nonflammable adhesive was necessarily terminated at this juncture due to the exhaustion of available time and funding.

PRESSURE SENSITIVE TAPE

Pressure-sensitive adhesives are composed of elastomeric or resinous polymers, to which are added tackifiers, plasticizers, fillers and stabilizers. Elastomeric polymers are by far the most widely used substrate polymer due to their superior basic properties. Since the properties of the pressure-sensitive adhesive vary directly with those of the base polymer, the choice of elastomer is critical. Properties such as specific adhesion to backing and substrates, water-and-moisture-resistance are required, along with the inability to support combustion under the conditions specified previously.

Since the base polymers themselves have little or no inherent tack and adhesive characteristics, tackifiers are necessary to enhance them (qualitatively and quantitatively). Due to the flammability requirements imposed for the subject application, the commonly-used, flammable tackifiers cannot be used. Consequently, a nonflammable compound had to be found which would be effective in tackifying the nonflammable base polymer.

As the tackifying agent is gradually added to the base polymer, tack increases through a maximum in the system and with further additions, tack decreases and finally disappears. As a result, the concentration of tackifier in the pressure sensitive adhesive is critical.

Plasticizers are also sometimes used in pressure sensitive adhesives in small concentrations. These materials tend to flexibilize the adhesive for improved low temperature properties. Unfortunately, the cohesive and adhesive strength is decreased.

Inert, reinforcing fillers can also be utilized, if necessary, to increase cohesive strength at a cost of drastic tack reduction. Other additives, in small concentration, may also be used for specific purposes such as antioxidants, ultraviolet inhibitors, etc.

Since a nonflammable elastomer suitable for a pressure sensitive adhesive base polymer was not available, it was necessary to select or prepare the required polymer. A linear fluorinated polyurethane (Polymer I) was prepared and examined. The resulting thermoplastic polymer showed poor elastomeric properties. Shear degradation of this material on a rubber mill did produce some tackiness, but not of a permanent nature. Compounding with low molecular weight Viton also yielded a tacky system, but adhesive and cohesive strength were poor. As a result, this particular material was dropped from consideration as the base polymer.

It is firmly believed that a further improved adhesive system based on Polymer A can ultimately be developed, since important variables such as stoichiometry, molecular weight, cure cycle, catalysts, and additives have not been fully studied under current funding. Work on the permanent bonding nonflammable adhesive was necessarily terminated at this juncture due to the exhaustion of available time and funding.

PRESSURE SENSITIVE TAPE

Pressure-sensitive adhesives are composed of elastomeric or resinous polymers, to which are added tackifiers, plasticizers, fillers and stabilizers. Elastomeric polymers are by far the most widely used substrate polymer due to their superior basic properties. Since the properties of the pressure-sensitive adhesive vary directly with those of the base polymer, the choice of elastomer is critical. Properties such as specific adhesion to backing and substrates, water-and-moisture-resistance are required, along with the inability to support combustion under the conditions specified previously.

Since the base polymers themselves have little or no inherent tack and adhesive characteristics, tackifiers are necessary to enhance them (qualitatively and quantitatively). Due to the flammability requirements imposed for the subject application, the commonly-used, flammable tackifiers cannot be used. Consequently, a nonflammable compound had to be found which would be effective in tackifying the nonflammable base polymer.

As the tackifying agent is gradually added to the base polymer, tack increases through a maximum in the system and with further additions, tack decreases and finally disappears. As a result, the concentration of tackifier in the pressure sensitive adhesive is critical.

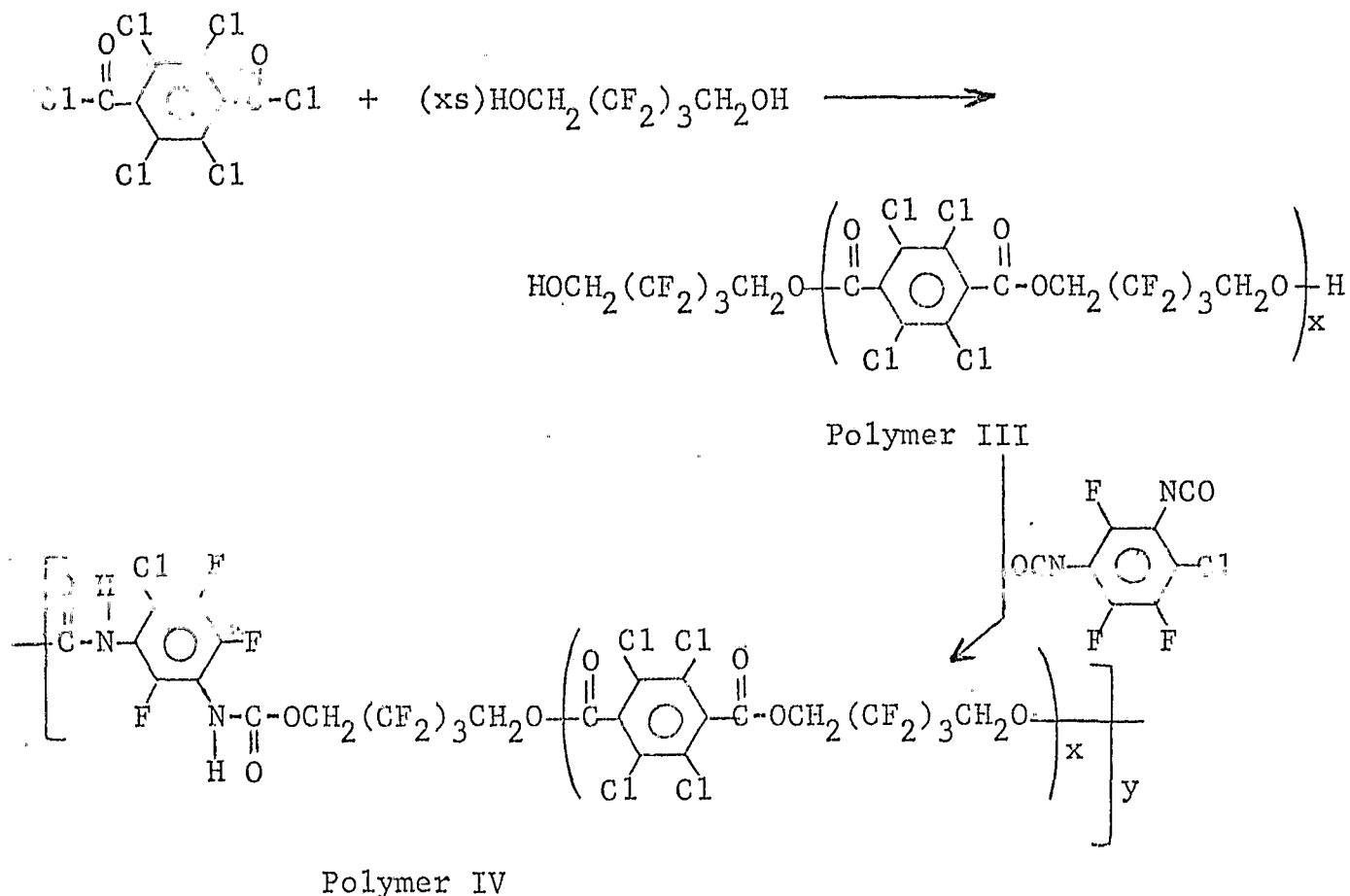
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A linear fluorinated polyurethane-polyurea (Polymer A) was prepared from Prepolymer II and Prepolymer III. However, the physical properties of the resultant thermoplastic material were disappointing. There was only a slight amount of "snap" and poor tear strength. This product showed only limited promise as a base elastomer for the pressure sensitive adhesive.

In an effort to upgrade the toughness and strength of the fluorinated polyurethane, a highly halogenated polyester-based polyurethane was prepared as follows.



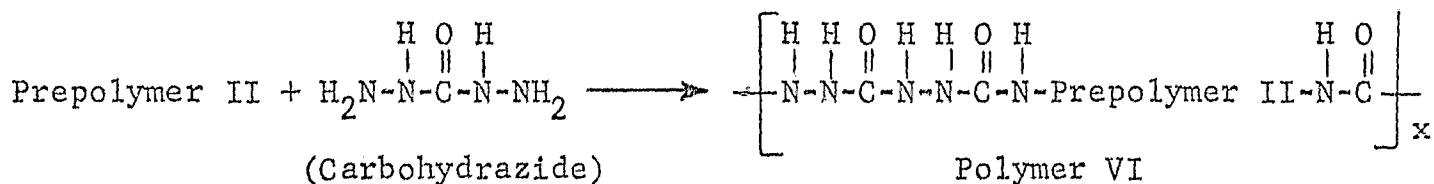
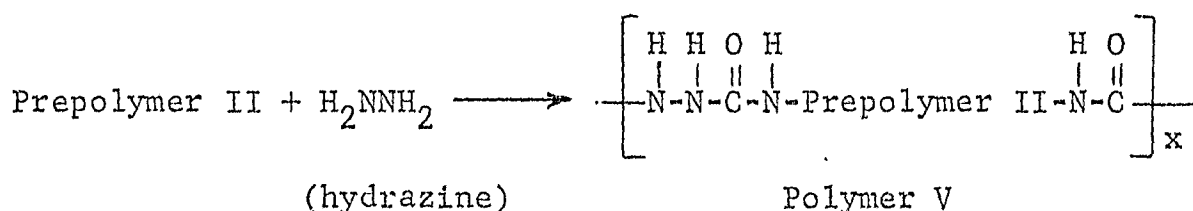
This brittle, high melting Polymer IV was incorporated by milling into the linear fluorinated polyurethane (Polymer I) in varying amounts, resulting in a two-phase composite blend. There was a considerable increase in the apparent strength and toughness of the system up to approximately 40% polyester loading. When 50% polyester was used, the blend became more crystalline than was desirable. These blends possessed adequate strength and toughness, but insufficient tack. Attempts to tackify this system with the fluorinated hydroxyl-terminated polyether were unsuccessful. The only result from this treatment was a considerable loss of strength of the milled blend.

Based on the above investigations, it was deemed necessary to approach the preparation of a suitable base polymer from two directions.

1) Preparation of Block Polymers - These polymers would consist of a crystalline segment and an amorphous segment. The amorphous segment is represented by the low molecular weight fluorinated polyurethane (Polymer I), which contributes flexibility to the final polymer. The crystalline segment, represented by the halogenated polyester-urethane (Polymer IV), would contribute toughness and "snap" to the final polymer.

2) Hydrogen Bonding - Many types of polymer systems exhibit excellent physical properties such as elasticity, toughness, tear strength, etc., as a result of hydrogen bonding between polymer chains. It was believed that a small amount of an active hydrogen-containing material could be incorporated to provide some interchain bonding stabilization. Severe limitations are imposed, however, as to the degree and kind of compound which can be added, due to the superimposed nonflammability requirement.

A block polymer was prepared which was capable of hydrogen bonding by chain extension through hydrazide in the polymer backbone. Polymer V was prepared by reacting Prepolymer II with hydrazine, while Polymer VI was made by reacting Prepolymer II with carbohydrazide as follows:



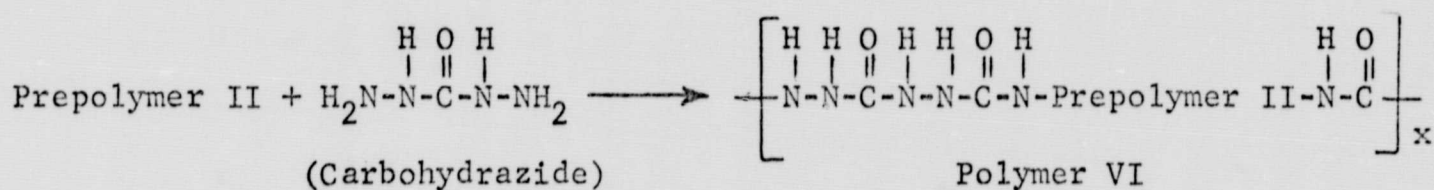
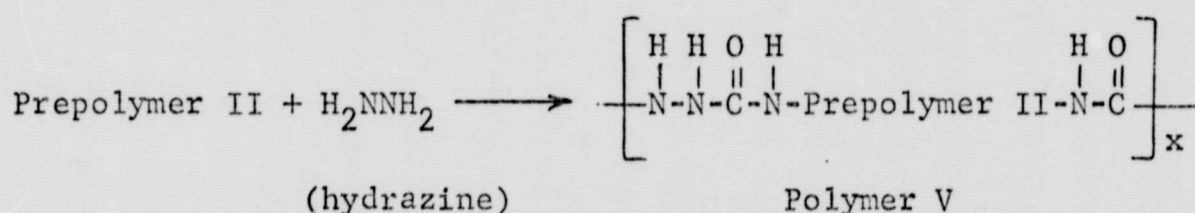
Polymers V and VI have two different degrees of hydrogen bonding capability. Both materials, which had to be prepared on a rubber mill to secure adequate mixing before gellation, were highly viscous systems with no appreciable snap or strength. Consequently, these materials were not examined further.

An attempt was made to prepare Polymer VII containing Polymer III as the crystalline segment as follows.

1) Preparation of Block Polymers - These polymers would consist of a crystalline segment and an amorphous segment. The amorphous segment is represented by the low molecular weight fluorinated polyurethane (Polymer I), which contributes flexibility to the final polymer. The crystalline segment, represented by the halogenated polyester-urethane (Polymer IV), would contribute toughness and "snap" to the final polymer.

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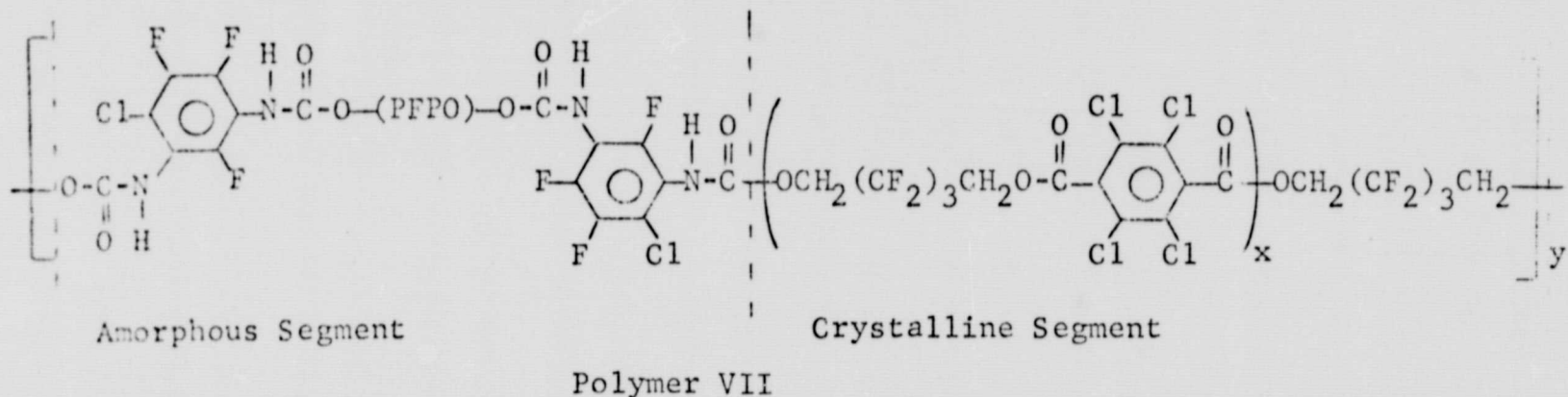
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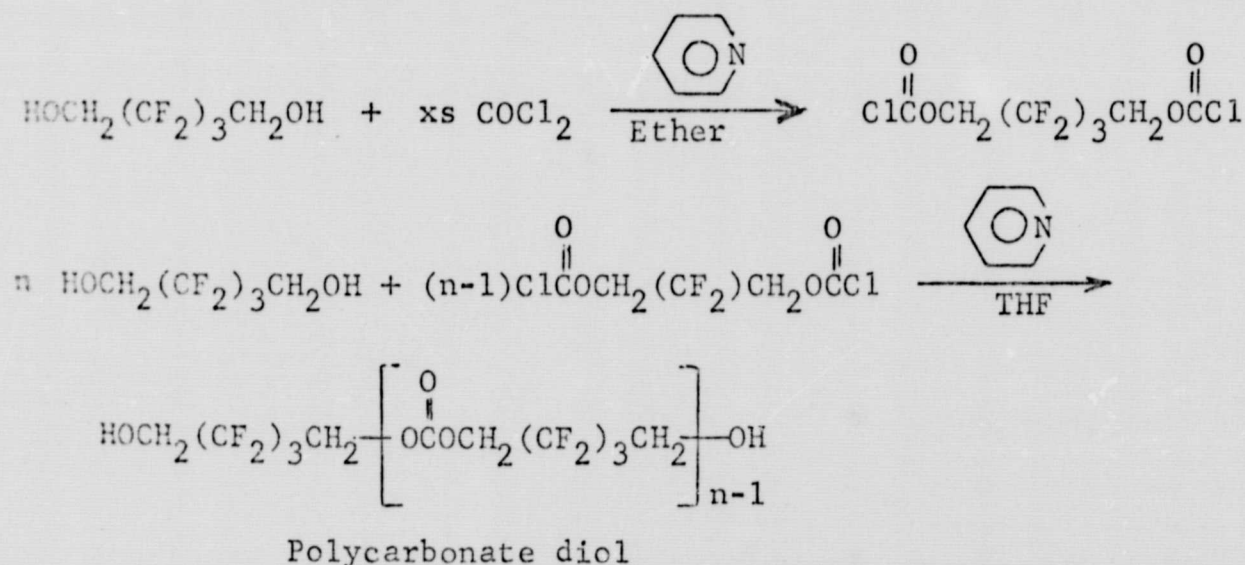
An attempt was made to prepare Polymer VII containing Polymer III as the crystalline segment as follows.

Polymer III + Prepolymer II
(molecular weight 1310)



Unfortunately, the two materials were not sufficiently compatible to permit any appreciable reaction to occur, even after 16 hour treatment at 225°C. The resultant product showed poor elevated temperature properties. Consequently, this system was abandoned.

Previous research in our laboratories has shown that the crystalline polycarbonate of hexafluoropentanediol was suitable for use in preparing elastomeric products.* Consequently, this compound was selected for investigation as the crystalline segment of the base polymer. The requisite diol-terminated polycarbonate prepolymer was prepared in three molecular weight ranges as follows:



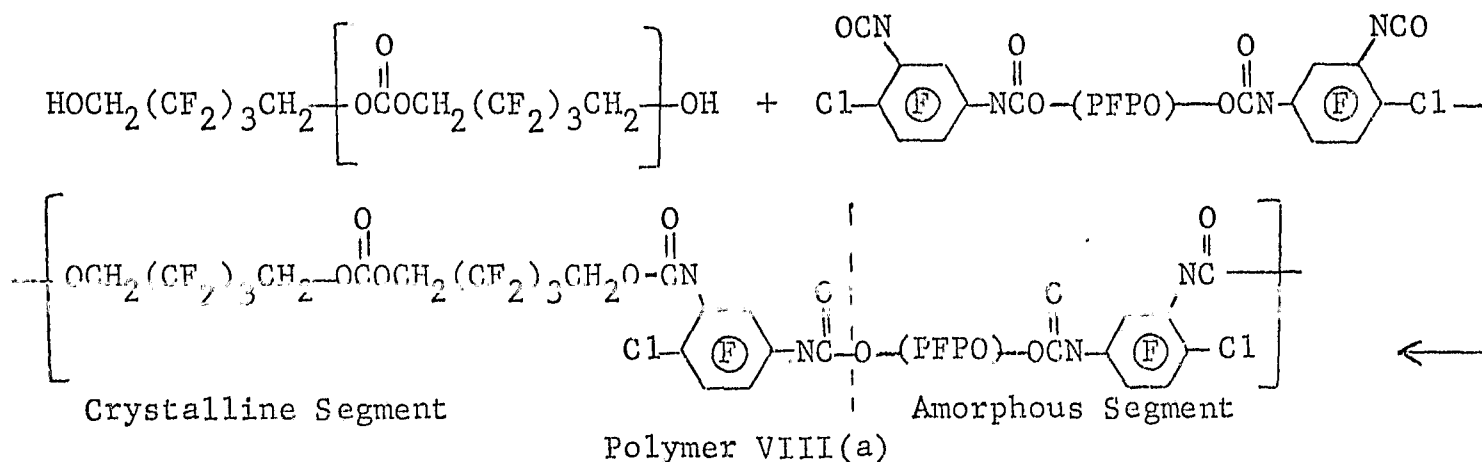
* Unpublished work

TABLE IV

AVERAGE MOLECULAR WEIGHTS OF THREE
POLYCARBONATES OF HEXAFLUOROPENTAMETHYLENE DIOL

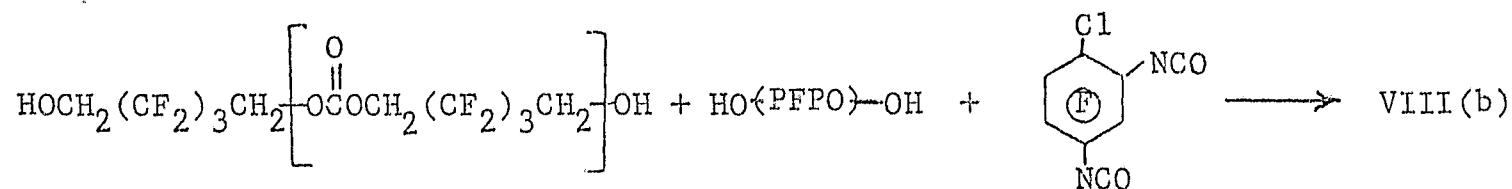
<u>n</u>	<u>Theoretical Molecular Weight</u>	<u>Molecular Weight by VPO (THF)</u>
2	688	715
3	1164	1170, 1160
4	1640	1638, 1630

The block copolymer (Polymer VIII) was then prepared in two ways; first by reacting the polycarbonate diol with Prepolymer II to give an ordered copolymer as shown below.



The resulting polymer was obtained as a translucent, tough, elastomeric solid.

The second method of preparation of Polymer VIII was as the random reaction product of the polycarbonate and hydroxyl-terminated polyperfluoropropylene oxide with chlorotrifluoro-m-phenylene diisocyanate as follows.



Polymers VIII(a) and VIII(b) are similar except that, in the former case, the crystalline and amorphous segments alternate, and in the latter case these segments are combined in a random fashion. While both of these

methods resulted in polymers with similar properties, and both types of materials were evaluated for pressure sensitive adhesives. The VIII(b) polymer was preferred on the basis of simplicity of preparation, and because there is a lesser chance of forming undesirable allophanate crosslinks by this method.

Flammability tests on polymer VIII were conducted at 6.2 psi-100% oxygen environments. The results of these tests showing the effect of three different molecular weight range polycarbonate segments is shown in Table V.

TABLE V
FLAMMABILITY TESTS ON POLYMER VIII
(6.2 psi 100% Oxygen)

	Molecular Weight of Polycarbonate Segment	% Polycarbonate Segment in Polymer	Burning Rate, in/sec	Distance Burned, inches
VIII-1	688	22.5	--	2.25
VIII-2	1164	35.5	--	3.0
VIII-3	1640	41.0	0.31	--

These flammability results were unexpected on Polymer VIII since a previous sample (120-88A) of formulated pressure-sensitive adhesive (Polymer VIII and tackifier) was self-extinguishing under both these conditions and 16.5 psi-60/40 oxygen/nitrogen. It is, therefore, unfortunate that these results were not obtained until after the available starting materials and adhesive formulation were committed to the use of this polymer system. The incorporation of relatively large amounts of nonflammable tackifier may, however, result in a self-extinguishing system as indicated previously.

A study of pressure-sensitive adhesive formulations was conducted using various modifications of Polymer VIII, and the tackifiers shown in Table VI. Of the original tackifiers studied (1 through 6) only PFPO imparted any degree of tack to Polymer VIII. While good tack was obtained with this system during blending, it was quickly lost upon cessation of mixing. For example, when the block copolymer and tackifier were thoroughly mixed, tack was lost within about 1 hour after mixing was stopped. When mixing was less complete, tack life was appreciably extended. It has also been observed that tack can be restored by additional mixing, particularly under high shear conditions, as in a rubber mill.

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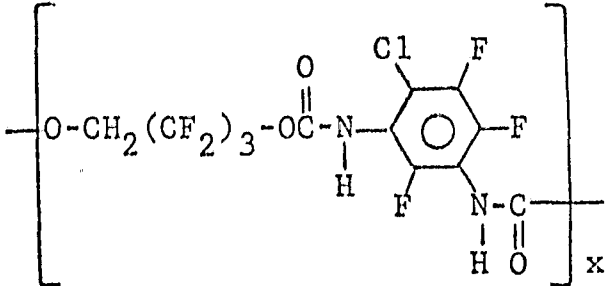
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(6.2 psi 100% Oxygen)

	Molecular Weight of Polycarbonate Segment	% Polycarbonate Segment in Polymer	Burning Rate, in/sec	Distance Burned, inches
VIII-1	688	22.5	--	2.25
VIII-2	1164	33.3	--	3.4
VIII-3	1640	41.0	0.31	--

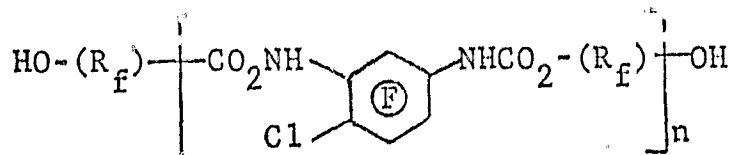
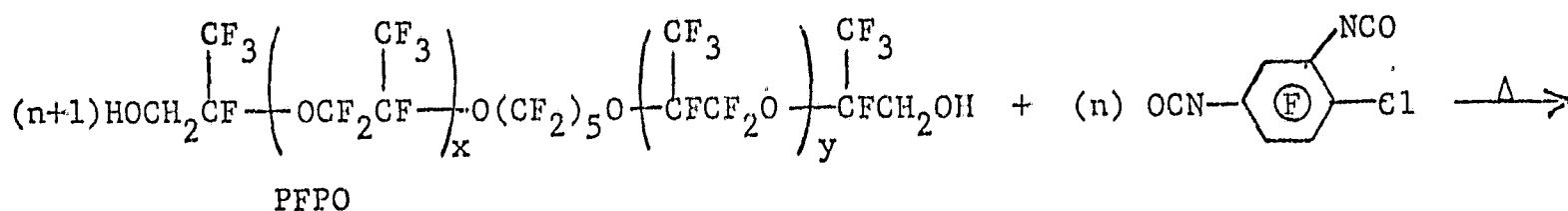
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TABLE VI
TACKIFIERS FOR PRESSURE SENSITIVE ADHESIVE

<u>Type</u>	<u>Concentration Range, pph</u>	<u>Comments</u>
1 	5-15	No tack
2 Nitroso Rubber 45 CF₃NO 5 C₆F₅NO 50 C₂F₄	5-10	No tack
3 Polycarbonate of Hexafluoro- pentamethylenediol, 1700 MW	5-15	Almost no tack
4 Polycarbonate of Hexafluoro- pentamethylenediol, 1200 MW	5-15	Almost no tack
5 Polycarbonate of Hexafluoro- pentamethylenediol, 700 MW	5-15	Almost no tack
6 Poly(perfluoropropyleneoxide) diol (PFPO), 1500 MW	5-15	Initial tack, however PFPO is more of plasti- cizer than tackifier
7 PFPO Chain Extended n = 1	5-29	Good initial tack, best about 20 pph
8 PFPO Chain Extended n = 2	10-25	Excellent initial tack, best about 25 pph, minimum permanent tack
9 PFPO Chain Extended n = 4	40-100	Excellent initial tack, reasonable tack retention, best tack near 50 pph

It appears, therefore, that mixing and shearing may be causing the rupture of weak inter-molecular (interchain) bonds. Alternatively, the uncoiling of molecules may be occurring to form a tacky system. When the mechanical energy is removed, following such a disturbance, the system may be free to return to a "ground state" with little or no tack. PFPO, as an oily liquid, apparently acts more as a plasticizer than as a tackifier in this ground state. Since it has no tack of its own, PFPO cannot itself impart permanent tack to the system. It was, therefore, felt that a higher molecular weight diol-terminated polyether with inherent tack of its own might impart the required permanent tack. Since these high molecular weight diols were not readily available, chain-extended diols (IX) using PFPO and chlorotrifluoro-m-phenylene diisocyanate chain extender, were prepared to achieve the same end. These derived polymers, IX, shown in the following equation, had the desired inherent tack, but were of lower viscosity than anticipated. For example, for the prepolymer where $n=1$, the material was readily pourable, while the $n=4$ material requires heating to provide sufficient flow for pouring.



Chain Extended PFPO (IX)

Pressure-sensitive adhesive formulations of IX ($n=1, 2$ and 4) thoroughly blended with VIII were prepared. These formulations all exhibited excellent initial tack. For example, one formulation removed paint from a metal surface. As before, however, most of this tack was lost shortly after mixing had ceased. It was observed that the permanent tack increased as the average n -value increased from 1 to 4 ; or, as the mechanical strength of the chain-extended diol (IX) increased. It, therefore, appeared that the permanent tack results from the inherent tack of IX. VIII is merely supplying mechanical strength to the system. Compositions with values of n greater than 4 were not studied, as it was felt that these materials were far too viscous for use with hand pressure.

A final adhesive formulation of 50 PBW of chain-extended diol VIII with $n = 4$ and 100 PBW of VIII ($1:1:1.8$ mole ratio, 1164 MW polycarbonate of hexafluoropentamethylene diol: 1480 MW PFPO:chlorotrifluoro-*m*-phenylene diisocyanate) was selected on the basis of residual tack and strength.

Mechanical test data obtained from the above adhesive formulation on β -glass is shown in Table VII, along with data obtained from a typical pressure-sensitive adhesive using PFPO tackifier.

TABLE VII

MECHANICAL PROPERTIES OF PRESSURE-SENSITIVE ADHESIVE

	TACKIFIER, Storage Time		
	Chain Extended Diol 1 Day	Chain Extended Diol 3 Weeks	PFPO, 1 Day
Butt-Tensile-to-Steel, psi	29	--	17
180° Peel-to-Aluminum, pli	3.2	1.75	1.5
Quick Stick, psi	--	--	8.5
Dead Load (1000 g/inch square), min	4.5	--	--

CONCLUSIONS

- 1) The optimum broad temperature range adhesive prepared on this program was based on Polymer A. It gave the best overall physical properties while maintaining acceptable nonflammable properties.
- 2) Polymer I possessed the required nonflammability characteristics for a broad range adhesive, but the elevated temperature performance was inadequate.
- 3) Additives to the Polymer I adhesive offered no significant improvement in nonflammability properties. In some cases, the product even became flammable.
- 4) While Polymer C had excellent properties as a broad range adhesive at elevated temperatures, the flammability properties were unacceptable.
- 5) Prepolymer II, cured with trifunctional nonhalogenated curing agents, such as trimesate, Mondur TM and PAPI were unacceptable as broad range adhesives due to a poor reaction rate or to flammability in the final products.
- 6) Phosphorus triisocyanate and phosphoryl triisocyanate may result in adhesives with unusual properties, but this effect has not yet been demonstrated.
- 7) Polymer VIII, tackified with a chain-extended polyether of perfluoropropylene oxide, produced the optimum pressure sensitive adhesive developed on the program. A more complete study of this system should result in improved fire resistant properties and an improvement in the peel strength of the adhesive.
- 8) Polymers A, IV, V, VI and VII are unsatisfactory as a base polymer for the pressure sensitive adhesive system due to poor physical properties.

RECOMMENDED FUTURE WORK

Additional studies of the permanent bonding adhesive system should include a further effort to develop a superior curing agent for the fluorinated isocyanates and their corresponding derivatives. These efforts should be concentrated in the areas of trifunctional materials and aromatic amines, paralleling current efforts on the related NASA-LOX compatible elastomer program.

Further work on the Polymer A can be expected to further enhance this system's performance since only a modest effort on its development has been possible to date. Areas requiring improvement include: 1) the short pot life of the adhesive system; and, 2) the relatively low bond strengths at elevated temperatures. Both can be improved with an optimized cure mechanism.

Additional development of a pressure-sensitive adhesive will require a superior nonflammable base polymer, since the polycarbonate-PFPO block copolymer which has been used above has been shown to be borderline with respect to flammability, particularly in high concentrations of the polycarbonate segment. The most likely possibility for such an improved system would be a system with lower polycarbonate segment concentration in the copolymer. Alternatively the polymer systems used for the permanent bonding adhesive could be subjected to additional modification for building a system with extended tack.

Follow-on efforts on the pressure-sensitive adhesive should include the study of different additives, as well as the use of several molecular-weight levels of the chain-extended polyether diol in the same adhesive formulation.

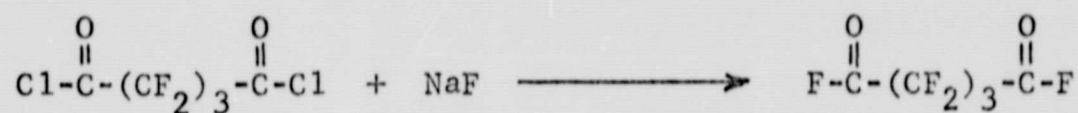
It is felt that these goals are well within reach, especially with the parallel rate of development of related systems under the separate NASA contract.

EXPERIMENTAL

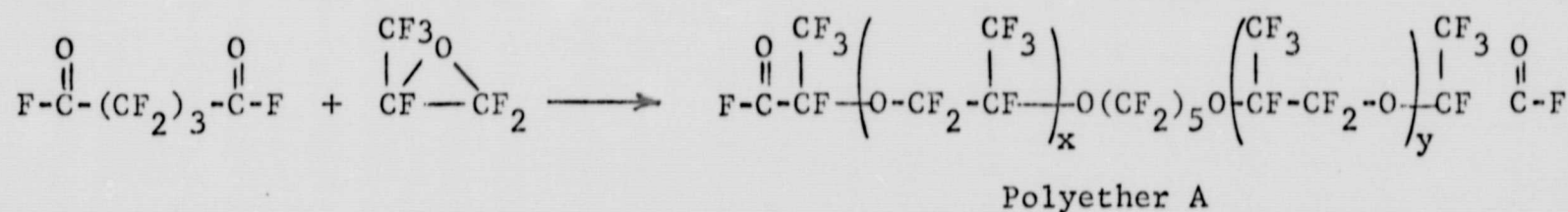
PREPARATION OF PREPOLYMER II AND PREPOLYMER III

The steps in the preparation of these products are as follows:

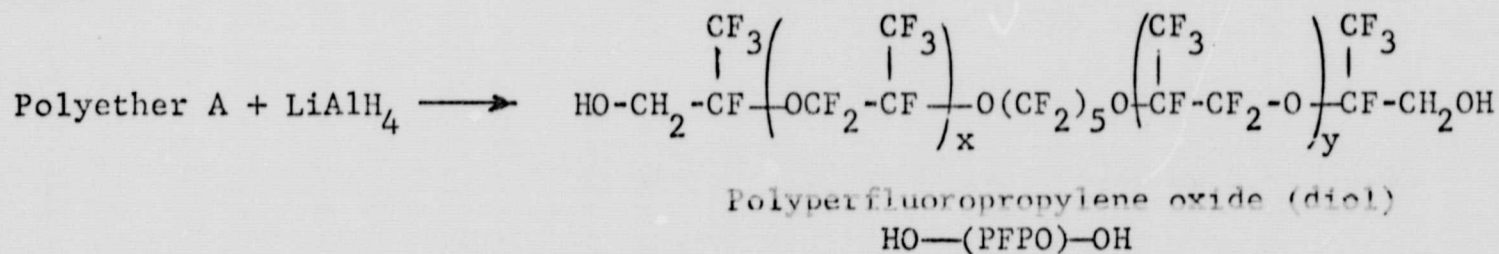
Step 1



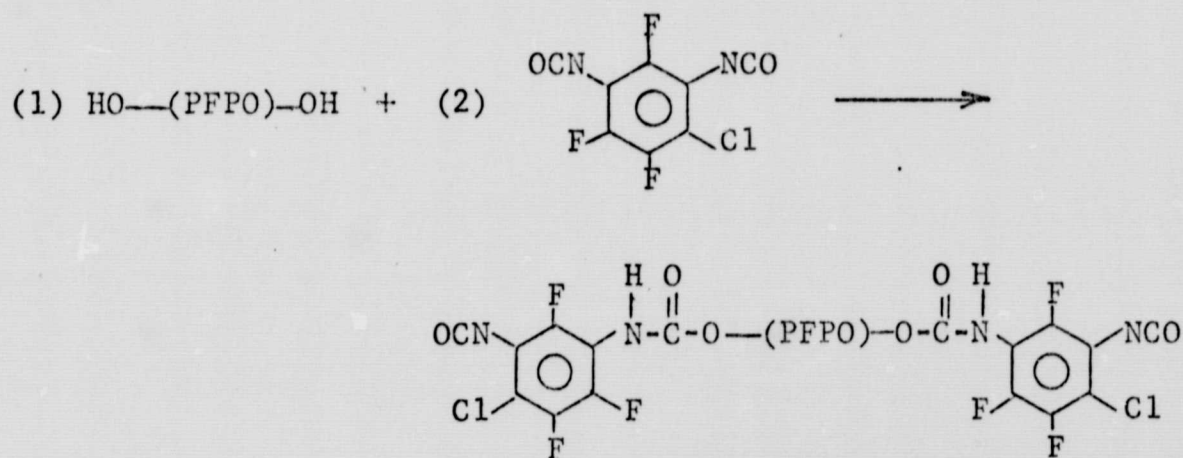
Step 2



Step 3

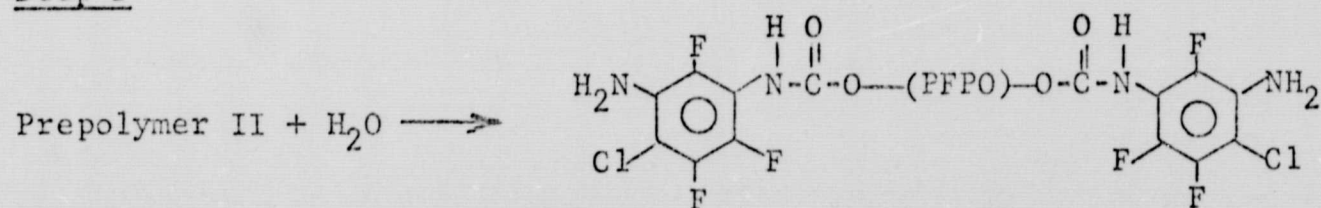


Step 4



Prepolymer II

Step 5



Prepolymer III

Steps 1-4 were developed for NASA-Huntsville under Contract NAS8-11068, (2) and subsequently scaled up under this program. Steps 1-2 have been scaled up to produce 5 pounds of material in Step 2 per run. Step 3 has been scaled up to produce 2 pounds of product per run. Several recent yields of Step 2 and 3 are shown in Table VIII.

Step 5 is conducted as follows: The product from Step 4, 720 g, was dissolved in 9 liters of tetrahydrofuran (THF) and 720 ml of water added. The THF and water were removed and the product chemically dried to yield 530 grams of product.

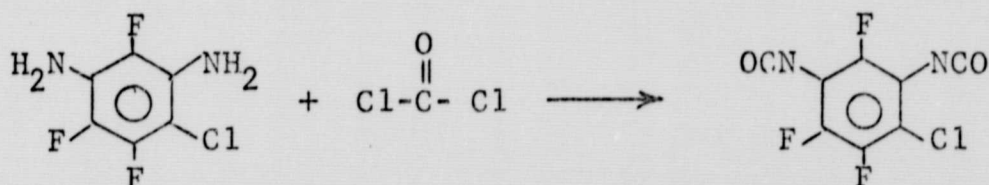
TABLE VIII

RECENT YIELDS OF POLYPERFLUOROPROPYLENEOXIDE DIOL

Hexafluoropropyleneoxide, grams	Perfluoroglutryl Fluoride, grams	Yield, grams	Molecular Weight
2000	231	472	950
2528	289	744	1480
1280	146	536	1700
2000	231	1039	1300

1-CHLORO-3,4,5-TRIFLUORO-m-PHENYLENE DIISOCYANATE

This compound was prepared as follows:



The procedure for preparing this compound was also developed for NASA-Huntsville under Contract NAS8-11068, (2) and subsequently scaled up on this program to produce one pound of product per run. Several recent yields are shown in Table IX.

(2) The Development of Structural Adhesive Systems Suitable for Use with Liquid Oxygen, Summary Report VI, Contract NAS8-11068, Dec 1968.

TABLE IX

RECENT YIELDS OF 1-CHLORO-3,5,6-TRIFLUORO-
m-PHENYLENE DIISOCYANATE

Moles	Yield, grams	Percent of Theoretical
4.5	≈ 550	≈ 58
5.5	≈ 450	≈ 41
5.5	≈ 640	≈ 58
5.0	≈ 400	≈ 40

INSTRUCTIONS FOR USE OF POLYMER A PERMANENT BONDING ADHESIVE

Storage: Component A-1 is sensitive to moisture and must be stored in a container with a dessicant. Since long-term storage data are incomplete, the product should be used as soon as possible after receipt. Low-temperature storage is recommended as an alternate. Care must be exercised, however, in allowing the product to return to room temperature before opening.
Component A-2 should be stored in an air-tight container.

Caution: The chemical, physical and toxicological properties of this product have not been fully investigated and its handling or use may be hazardous. Exercise due care.

Mixing

Instructions: This polymer system has a short pot life (about 10 minutes). As a result only sufficient adhesive should be mixed for immediate needs. Component A-2 should be warmed to 120°-160°F and mixed thoroughly prior to use.

The mixing ratio shall be 19.0 parts of Component A-1 and 12.0 parts of Component A-2. Mixing should be continued until the components are homogeneous (about 2 minutes).

Application Procedure:

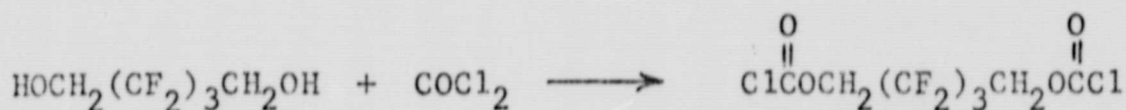
The adhesive consistency is suitable for application with a trowel or spatula. Care should be exercised to compensate for the short pot life of the adhesive.

Curing

Procedure: Bonding fixtures or vacuum bag pressure (0.5 atm. Max) may be used as dictated by the specific application. The recommended cure cycle is overnight heating at 160°F plus 8 hours at 250°F.

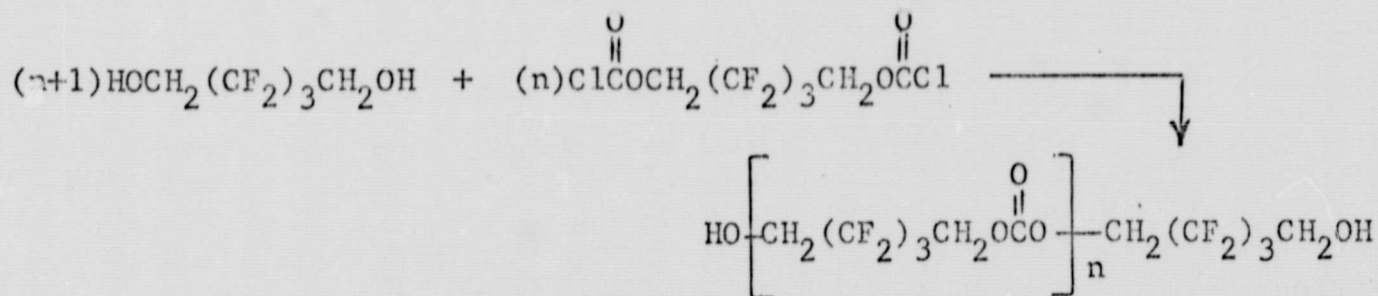
PREPARATION OF PRESSURE SENSITIVE ADHESIVE TAPE

Step 1 - Preparation of Hexafluoropentamethylene-bischloroformate



Phosgene (450 g, 4.5 mole) was condensed into diethyl ether (8 liters) at $-10-0^\circ\text{C}$. Pyridine (332 g, 4.2 mole) was then added over a period of 30 minutes with rapid stirring, producing a slurry of chlorocarbonyl-pyridinium chloride. Hexafluoropentanediol (424 g, 2.0 mole) in diethyl ether (1000 ml) was added over a 2-hour period and the temperature allowed to come to ambient. Stirring was continued for 4 hours. The reaction mixture was then filtered under dry nitrogen and allowed to stand overnight. The solvent was then removed from the clear solution under reduced pressure (40°C). Vacuum fractionation of the remaining mobile liquid was carried out. The fraction boiling between $82^\circ-86^\circ\text{C}$ at 2-4 mm was collected. Vapor phase chromatography indicated purity $>99.7\%$. Total yield was 326 g (48%).

Step 2 - Preparation of Hydroxyl-Terminated Polyhexafluoropentamethylene-carbonate



The following experimental data covers the case where $\text{n}=2$. It is typical of the other two preparations where $\text{n}=4$ and 6.

Hexafluoropentanediol (84.8 g, 0.40 mole) was dissolved in dry tetrahydrofuran (150 ml). Pyridine (32.4 g, 0.41 mole) was added and the mixture cooled to $\sim 5^\circ\text{C}$. Hexafluoropentamethylene-bischloroformate (67.4 g, 0.20 mole) in THF (50 ml) was added with stirring over a one-hour period. The temperature was kept at $<15^\circ\text{C}$ during the addition, then stirred overnight at room temperature. The slightly pink precipitate of pyridinium chloride was filtered off and the resulting water-white solution was poured into one liter of water, which had been acidified with 20 ml of conc. HCl, and vigorously stirred. After settling, the aqueous layer was removed by decantations and the acid wash repeated. The viscous oil was then washed twice with distilled water (2 x 1000 ml). After the final water wash, the white viscous oil was taken up in THF and dried over MgSO_4 overnight. Following filtration and vacuum removal of solvent (at 90°C) a pale yellow

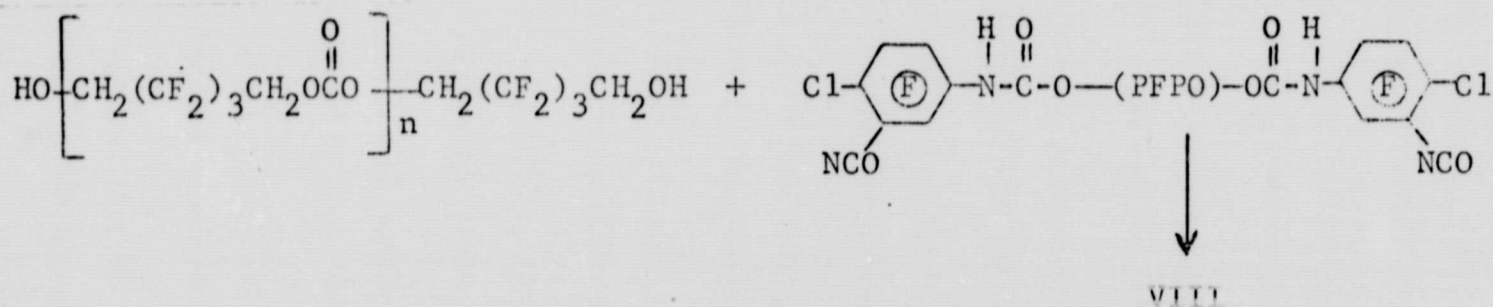
very viscous oil was obtained which slowly solidified over a period of a few days; yield 109.1 g (79.5%).

Vapor pressure osmometry showed the following results on the 3 pre-polymers:

<u>n</u>	<u>Molecular Weight Theory</u>	<u>Molecular Weight Found</u>
2	688	715
4	1164	1160, 1170
6	1640	1638, 1630

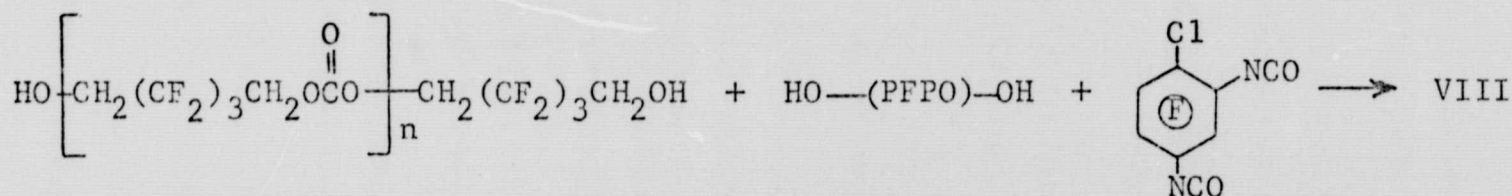
Step 3 - Preparation of Block Copolymer

Method 1 - Ordered Polymer



Hydroxyl-terminated poly(hexafluoropentamethylenecarbonate) (688 molecular weight, 34.6 g, 0.0495 mole) and Prepolymer II (1977 molecular weight, 89.0 g, 0.045 mole) were placed in a resin pot equipped with stirrer and nitrogen atmosphere. Mixing was started at 70°C with subsequent slow heating to 120°C. The reaction mixture was held at 120°C overnight. The extended-polymer product was a tough, flexible mass with a theoretical molecular weight of 27,500.

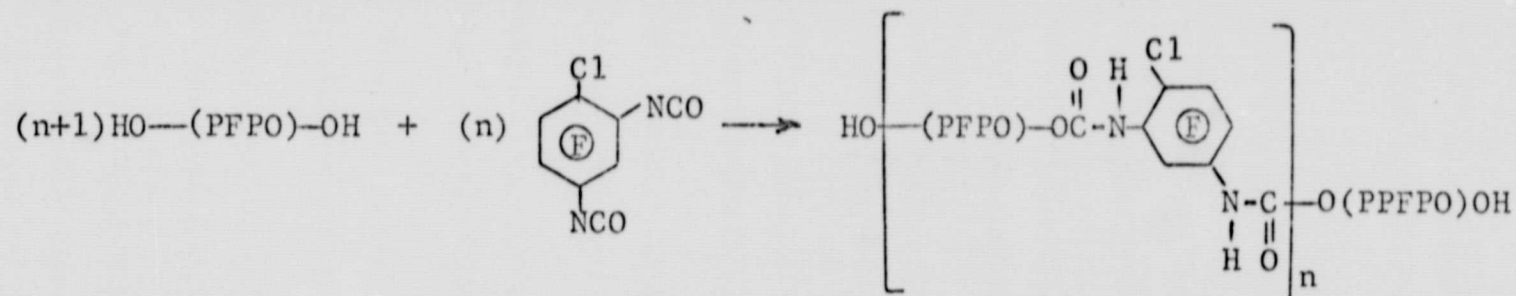
Method 2 - Random Polymer



Hydroxyl-terminated poly(hexafluoropentamethylenecarbonate) (1164 molecular weight, 58.25 g, 0.05 mole), polyperfluoropropyleneoxide diol (1480 molecular weight, 74.0 g, 0.05 mole) and 1-chloro-3,5,6-trifluoro-m-phenylene diisocyanate (22.4 g, 0.09 mole) were combined in a resin pot

equipped with stirrer, condenser and nitrogen atmosphere. The reaction mixture was heated slowly to 80°C and held for 2 hours at this temperature. One drop of stannous octoate catalyst was added and the reaction mixture was heated to 110°C and held for 2 additional hours. The product was a tough, flexible polymer with a theoretical molecular weight of 15,500.

Step 4 - Preparation of Chain-Extended PPFPO



The following procedure is for n=4. Other molecular weights with different values of n are prepared by appropriately modifying the stoichiometry.

Polyperfluoropropyleneoxide-diol (1480 molecular weight, 37.0 g, 0.025 mole) and 1-chloro-3,5,6-trifluoro-m-phenylene diisocyanate (5.0 g, 0.020 mole) were combined in a resin pot equipped with a stirrer, condenser, and nitrogen atmosphere. The reaction mixture was heated to 82°C over a period of 30 minutes. One drop of stannous octoate catalyst was added and the mixture held between 80° and 100°C for an additional 45 minutes. The product was a viscous liquid with no isocyanate bonds visible in the IR.

Step 5 - Preparation of Pressure-Sensitive Adhesive

The block copolymer (60 g) from Step 3 random method was mixed with the chain extended diol (n=4, 30 g) from Step 4 on a rubber mill until no change was evident. The resultant pressure sensitive adhesive was then applied to β-glass with mild heating; Teflon tape being applied to the exposed surface for release purposes.