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DEVELOPMENT OF MODIFIED POLY(PERFLUOROPROPYLENEOXIDE) URETHANE SYSTEMS FOR USE IN LIQUID OXYGEN AND IN ENRICHED 100% OXYGEN ATMOSPHERE

by E. S. Harrison

WHITTAKER CORPORATION
Research and Development Division

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16. Abstract This program consisted of two separate though related phases. The initial phase was directed toward improving the mechanical and adhesive properties of the very highly fluorinated-polyurethane resin system derived from the hydroxyl-terminated polyperfluoropropylene oxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate. Various new curing agents for this system were investigated, with the goal of providing a more thermally stable crosslink (cure) mechanism to provide wider applicability and fuller utilization of the outstanding oxygen resistance of the PFPO system. Significant improvements in reproducibility and overall bulk elastomeric properties have been achieved with only moderate improvement in the elevated temperature (94°C) adhesive performance. Complete resistance to liquid- and gaseous-oxygen impact at pressures as high as 1035 N/cm^2 have been attained with the use of the PFPO resin castings. This high pressure insensitivity is of particular importance in many potential applications. Thus the polyurethane system holds an essentially unique position as the material of choice in these critical areas. The second corollary phase was directed toward investigating the feasibility and optimization of the allophanate cured, urethane extended polymer derived from hydroxyl-terminated polyperfluoropropyleneoxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate, as the adhesive system for use in a weld-bond configuration for liquid oxygen tankage. This second phase followed a two-fold directive. First, to refine the synthesis and application procedures of the adhesive system to insure liquid oxygen compatibility (under 10 kg-m loading) and secondly, develop procedures and techniques to provide high quality weld-bonded joint configurations. Such refinements and developmental procedures have been successfully accomplished.

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FOREWORD

This report was prepared by Whittaker Corporation, Research and Development Division (WRD), under Contract No. NAS8-27087, Control No. DCN 1-9-54-20052(1F), entitled "Development of Modified Poly(perfluoro-propyleneoxide) Urethane Systems for Use in Liquid Oxygen and in Enriched 100% Oxygen Atmosphere", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Astronautics Laboratory, Materials Division, Nonmetallic Materials Branch, Polymer Chemistry Section with Mr. D. M. Kornfeld acting as project officer.

The research work was conducted in WRD's Polymer Research Department under the direction of Chadwick B. Delano, Acting Manager. Mr. Edward S. Harrison was the principal investigator. Also contributing to the program was Mr. William D. Warner. Analytical work was carried out by Dr. William G. Stevens.

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Edward S. Harrison

Approved by: Chadwick B. Delano

Chadwick B. Delano

SUMMARY

This program consisted of two separate though related phases. The initial phase was directed toward improving the mechanical and adhesive properties of the LOX-compatible poly-fluorinated polyurethane resin system derived from the hydroxyl-terminated polyperfluoropropylene oxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate.

Liquid oxygen compatibility is defined in MSFC-SPEC-106B. The material must show no evidence of reaction (i.e., audible explosion, visible flash in a darkened room, discoloration or evidence of burning) when impacted at 10 kg-m in the pure oxygen environment.

Various new curing agents for this system were investigated, with the goal of providing a more thermally stable crosslink (cure) mechanism to provide wider applicability and fuller utilization of the outstanding oxygen resistance of the PFPO system.

The curing agents investigated included the following: cyanoguanidine, melamine, cyanuric trihydrazide, perfluoroalkyl ether substituted guanamines (both mono- and di-terminated) in various molecular weight ranges and combinations of these.

Significant improvements in reproducibility and overall bulk elastomeric properties have been achieved with only moderate improvement in the elevated temperature (94°C) adhesive performance).

Resistance to liquid- and gaseous-oxygen impact at pressures as high as 1035 N/cm^2 has been attained with the use of the PFPO resin castings. Sporadic incompatibility was, and still remains, a continuing problem on a batch-to-batch basis.

The second corollary phase was directed toward investigating the feasibility and optimization of the allophanate cured, urethane extended polymer derived from hydroxyl terminated polyperfluoropropyleneoxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate, as the adhesive system for use in a weld-bond configuration for liquid oxygen tankage.

This second phase followed a two-fold directive. First, to refine the synthesis and application procedures of the adhesive system to insure liquid oxygen compatibility (under 10 kg-m loading) and secondly, develop procedures and techniques to provide high quality weld-bonded joint configurations.

Emphasis was placed on preparative and purification techniques for the basic polymer system. Throughout the entire program these efforts were necessary, inasmuch, as a few (1-2/20 specimens) reactions with liquid oxygen at 10 kg-m impact was found in the preliminary syntheses. Refinement in technique and procedures has further decreased the low level incompatibility problem.

Concurrent with the improved compatibility a surprising reduction in adhesive strength was found. A commercial primer system (DC-1205) was found which surmounted the problem and in fact considerably improved adhesive performance.

Weld-bond studies included both weld-through of uncured adhesive and capillary fill-in of previously spotwelded adherends. Both techniques provided acceptable results. Superior adhesive performance was demonstrated when the primer system was employed. However, the weld-through technique was initially disallowed by the high resistivities encountered in the combination of cured primer and uncured adhesive. This difficulty was readily overcome by adding a conductive filler to the adhesive.

High quality welds (and adhesive values) are, therefore, readily attained by both fabrication methods.

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PHASE I
INTRODUCTION AND OBJECTIVES

In previous studies [NAS8-11068 (1963-1968) and NAS8-24389 (1969-1970], Whittaker Research and Development Division (WRD) was successful in the development of a highly-fluorinated polyurethane system (PFPO) which showed useful adhesive, and related, properties from cryogenic to moderately elevated temperatures (66°C). The system was determined to be essentially insensitive to impact in liquid oxygen as defined by MSFC-SPEC-106B and to possess self-extinguishing characteristics in 100% oxygen atmosphere at 11.5 N/cm^2. Formulations were developed which demonstrated utility not only in adhesive applications but also exhibited feasibility as conformal coatings and electronic embedment compounds in oxygen-rich environments, typified by manned spacecraft atmospheres.

This resin system is based on a two-component prepolymer derived from the hydroxy-terminated polyether of perfluoropropylene oxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate.

Under the present contract, efforts were directed toward improvement of both bulk elastomeric properties and elevated temperature performance by incorporating alternate curing agents which would offer such improvements, without introducing deleterious effects on the excellent oxidation resistance.

PHASE I
TECHNICAL DISCUSSION

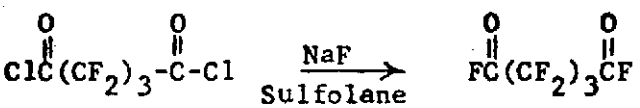
I - BASIC POLYMER SYSTEM

A. Preparation of Poly(perfluoropropyleneoxide)urethane System

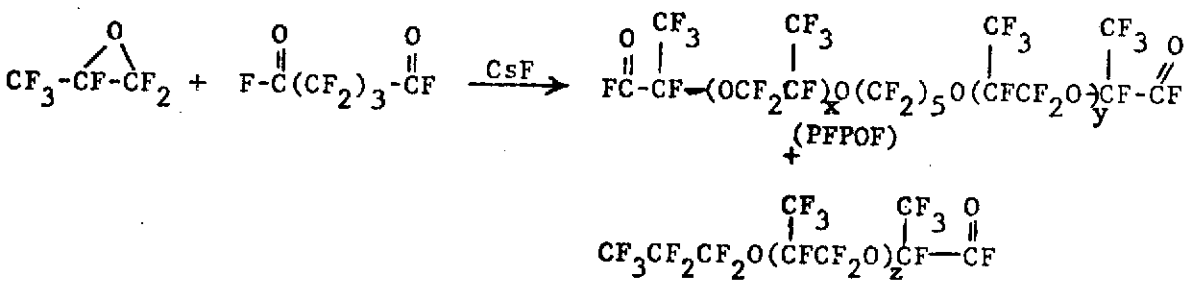
Although a detailed description of the preparation of the end basic polyurethane system has been provided in the preceeding summary report, the essential details have been repeated here for the sake of continuity and clarity. Experimental details of the optimized preparation are included in a later section.

The polymer is prepared through the following reaction sequence:

1) Preparation of perfluoroglutaryl fluoride

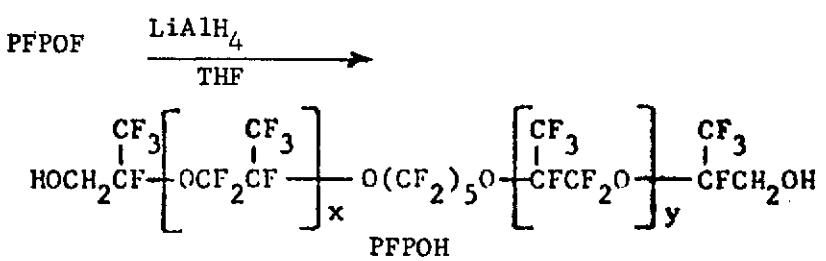


2) Preparation of diacylfluoride-terminated polyperfluoropropylene-oxide (PFPOF)

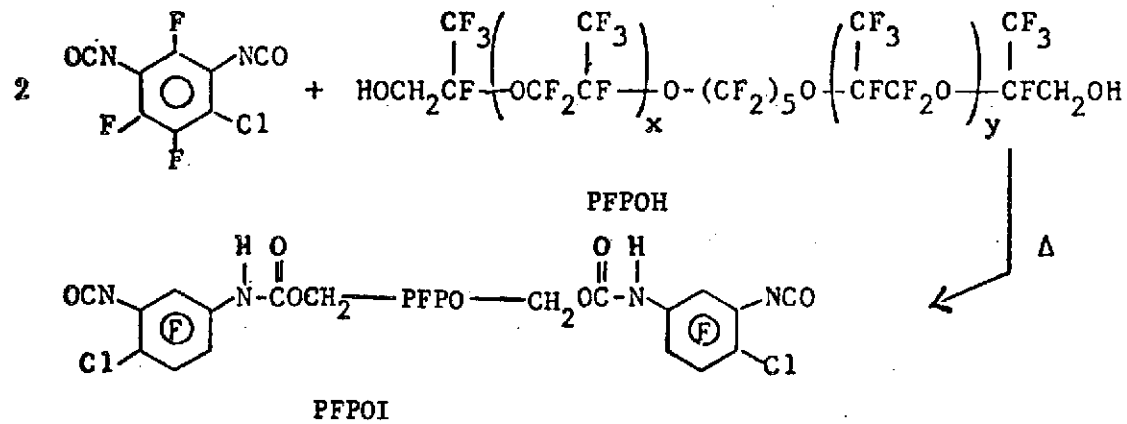


Followed by separation of higher molecular weight difunctional material.

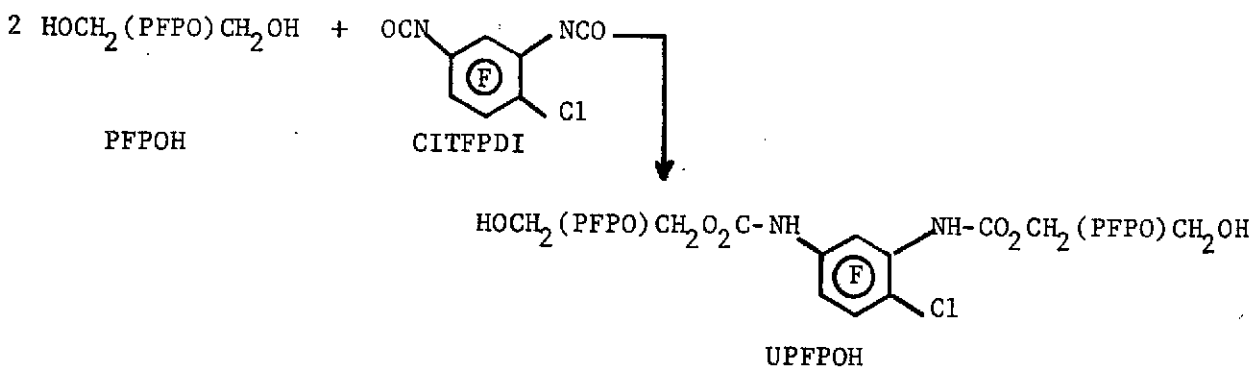
3) Preparation of hydroxyl-terminated polyperfluoropropylene-oxide (PFPOH)



4) Preparation of isocyanate-terminated polyperfluoropropyleneoxide (PFPOI)



5) Preparation of hydroxyl-terminated bis-urethane of polyperfluoropropyleneoxide (UPFPOH)



6) Preparation of the polyurethane:

(13) PFPOI + (1) UPFPOH $\xrightarrow{\Delta}$ Allophanate cured polyurethane with NCO/OH ratio of 1.8/1

B. Physical Properties

1. Bulk Properties of the PFPOI/UPFPOH System

A cast sample of the title system was cut into micro tensile specimens and the following properties determined:

Tensile Properties of PFPOI/UPFPOH Casting*

Temp	Tensile Strength N/cm^2 (psi)	Initial Modulus N/cm^2 (psi)	Elongation (%)	Hardness (Shore A-2)	Density (g/cc)
26°C	1990 (2890)	28,820 (41,800)	137	96	1.89

* Derived from PFPOF of 1210 mol. wt.

The system failed to show high recovery and elasticity characteristics, but it did exhibit satisfactory strength parameters for adhesive and conformal coatings applications.

2. Dielectric Testing

The use of the PFPOI/UPFPOH system shows great promise in specialized electronic applications in enriched oxygen atmospheres. Measurements of the electrical properties of the material were cursorily investigated.

Preliminary results at 10.2 GHz are quite promising. WRD believes that they are reliable and in line with those anticipated, based on analogy with other urethane and highly fluorinated polymer systems.

Dielectric Constant	2.19
tan δ	0.12
Power Factor	0.12

A sample of cured polymer was submitted to the Contracting Officer for audio- and radio-frequency dielectric measurements.

C. Adhesive Properties

Lap shear strength levels of bonds prepared from the derived allophanate-cured PFPO system have been shown to be reproducible, when cured at an overall NCO/OH ratio of 1.8/1.0. The adhesive system shows significant improvement in adhesive properties with variation in the molecular weight of the starting acid fluoride-terminated prepolymer PFPOF. These results are most readily interpreted by attributing those changes in tensile strength that are realized to minor variations in bulk modulus and tensile strength of the resin itself, induced by changes in the overall crosslink density and in the extent of "nonbonding" flexible perfluorooxyalkyl segments between the polar urethane/allophanate "bonding" sites. Typical properties are shown in Table I.

TABLE I

TENSILE SHEAR STRENGTH* OF
ALLOPHANATE-CURED PFPO ADHESIVE

Molecular Weight of Starting PFPOF	Lap-Shear Tensile Strength at Temperature, N/cm^2 (psi)		
	-196°C	RT	94°C
1360	4120 (5970)	1080 (1570)	206 (300)
1210	3120 (4530)	1850 (2690)	255 (370)

* F.P.L. etched (sodium dichromate/sulfuric acid) 2024-T3 clad aluminum. 0.004 in. glueline thickness. Cured 3 days at 82°C.

The difference in molecular weight (150 m.w. units) is effectively one monomeric unit of hexafluoropropylene oxide (m.w. 166). Hence, the effective crosslink density is increased and the inter-urethane distance is diminished, both by approximately 10 percent. Thus, the lower molecular weight system reflects these small differences by the responses seen in Table I, i.e., less flexibility at cryogenic temperatures, substantially greater bond strengths near the apparent T_g of the polymer, and little or no effect once the polymer has relaxed and softens to a great extent (94°C).

D. Oxygen Compatibility Testing

With the preparation of each batch of PFPOI/UPFPOH polymer a film was cast, samples prepared, and routinely submitted to NASA-MSFC for impact testing in liquid oxygen. Early in the program, a low degree of sensitivity was noted; i.e., one or two of each lot of 20 specimen samples failed at 10 kg-m impact.

These results were unexpected since testing of the same system on previous programs had shown PFPO-based resins to be completely compatible with liquid oxygen; i.e., 0/100 reactions. The low level of reaction hence indicated some slight degree of adventitious contamination from some undetermined source.

The observed low level and scatter could be attributed to several possible causes:

1) Particulate (dust) matter which would initiate detonation
2) Possible noncompatibility of the release agent used as a separator on the glass plate casting back-up
3) Thickness of sample
4) Possible contamination during processing

The preparation of the specimens was consequently repeated using more care to prevent contamination, again using a casting technique on plate glass "released" with GS-3 fluorocarbon release agent. The individual specimens were carefully inspected for dust particles under low power magnification. Some particulate surface particles were observed, which could, however, be removed by simple wiping techniques.

An additional 20-sample set was cast on a solvent cleaned Teflon surface, with the same inspection and cleaning techniques used.

The results of impact testing in liquid oxygen indicate that the detonations previously encountered may be attributable to an incompatible substance deposited on the film by the mold release. Thus, the samples cast on GS-3 released aluminum showed 3/20 detonations, the same low level initially encountered; whereas the samples cast on Teflon showed 0/20.

To verify these results, an additional fourth set was prepared using both techniques (i.e., Teflon vs. GS-3 released aluminum). The same low level of contamination was again found as evidenced by the one or two failures per 20 specimen set. Hence, no firm conclusion may be reached regarding the mold release contamination.

The entire procedure, from initial synthesis reactions through final sample preparation, was rigorously surveyed and suitable modifications made to preclude, or at least minimize, external contamination.

Since several steps are involved in the overall polymer synthesis and fabrication, an oversight of an unobvious source of contamination is probable. Failure to observe the most stringent restrictions may in fact result in possible introduction of the contaminant and cause unnecessary rejection of an entire batch of polymer.

The results of the survey uncovered only a very few possible sources of such contamination. The two most significant potential errors found were: (1) distillation impurities during the final vacuum distillation and purification of PFPOH (hydroxyl terminated polyperfluoropropyleneoxide) occasioned by use of wooden splints (rather than inorganic boiling stones) as a nucleating device to create smoother boiling and prevent "bumping" may possibly have served to introduce ligninous (flammable) residue; and (2) insufficient attention paid to scrupulous cleanliness and adherence to prescribed techniques in specimen preparation.

With these suspected potential trouble-spots corrected, the entire procedure was repeated through specimen preparation. The results this time were outstanding. Not only were both sets of specimens (cast on both Teflon- and on GS-3-released aluminum) found to be resistant to liquid oxygen at 10 kg-m impact, but also (remarkably) they showed no (0/40 and 0/40) reaction in both liquid and gaseous oxygen at 1035 N/cm^2 oxygen pressure. To WRD's knowledge the polyurethane system is the only adhesive which meets this most stringent requirement.

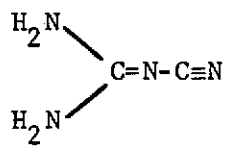
These results, however, are as yet not routinely attainable and hence batch-to-batch testing must be carried out.

II - ALTERNATE CURING SYSTEMS FOR ISOCYANATE-TERMINATED PERFLUOROPOLYETHER (PFPOI)

A. Cyanoguanidine as Curing Agent

1. Rationale of the System

Significant improvement in elevated temperature (200°F) performance of the PFPO resin system has been attained by utilizing cyanoguanidine as a curing agent.



The utility of this agent is predicated on its lack of the labile (oxidatively) carbon-hydrogen bonds. In addition, the reactivity of the amine functionality is greatly attenuated by resonance-stabilization and by the multiplicity of the possible tautomeric forms. Reduced reactivity is essential due to the extremely reactive nature of the derived fluoroaryl isocyanate.

Cure of the PFPOI (isocyanate-terminated polyperfluoropropyleneoxide) prepolymer proceeds at a reasonable rate only at temperatures in excess of ~160°C. The same latency of this catalyst at lower temperatures has long been noted in epoxy resin technology, and has generally been ascribed to the essential insolubility of the cyanoguanidine in the various resin systems. A corresponding lack of reactivity has currently been noted in the current PFPOI system. Thus, no significant degree of reaction is apparent after several hours at 121°C. The finely-divided curing agent obviously remains particulate and not appreciably dissolved.

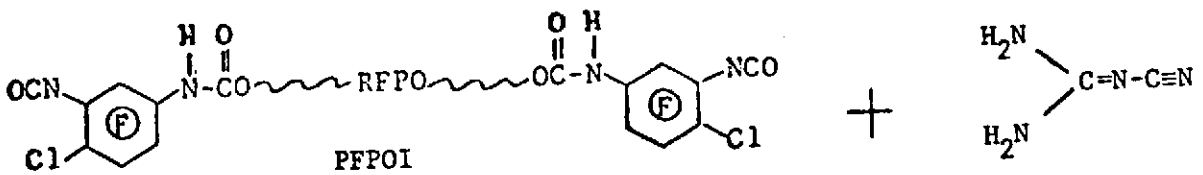
At higher temperatures (177°C), however, the resin/curing agent mixture clears and the ensuing cure is apparently complete in less than one hour at this temperature.

2. Bond Strengths

Tensile shear bonds were prepared using dichromate-etched aluminum in a standard bonding fixture. This brief study was designed to evaluate shear strength as a function of NCO/NH_2 ratio. An apparent maximum in this parameter occurs at a 1.3/1 ratio and represents a new high for room temperature strength of the PFPOI-derived systems (2010 N/cm^2). These data are presented in Table II.

TABLE II

CYANOGUANIDINE-CURED PFPOI



NCO^*/NH_2 Ratio	Lap-Shear Tensile Strength, N/cm^2 (psi)		
	-196°C	RT	94°C
1.1	575 (835)	1600 (2320)	720 (1045)
1.3	850 (1240)	2000 (2905)	717 (1040)
1.5	1060 (1535)	1910 (2765)	550 (798)
1.7	1120 (1625)	1520 (2210)	492 (714)

* Prepared from PFPOI derived from PFPOF of 1360 molecular weight.

These data indicate some brittleness for the cyanoguanidine-cured PFPOI systems at -196°C. Visual inspection of the failed specimens clearly indicated essentially 100% adhesive failure. Failures of this type are most generally obtained with the more brittle resin systems at cryogenic temperatures. The failures at room temperature and at 94°C are more typical of a tougher system, and are essentially 100% cohesive in nature.

The brittleness at cryogenic temperatures, while rather disappointing, can in all probability be overcome by the use of a multicomponent system, wherein more flexibility, as derived from additional chain mobility, has been incorporated.

3. LOX Compatibility Results

A significant drawback to a 177°C-cure is the facile hydrolysis of the isocyanate functionality by atmospheric and adventitious (adsorbed on the bonding substrate) moisture. Any hydrolysis generates a two-fold detrimental effect on stoichiometry, hence must be kept to a minimum. This problem is not nearly as severe in bonding operations as it is in film casting, since the total exposed area is minimal.

A continuous film has, however, been successfully cast in a dry nitrogen atmosphere. LOX-compatibility specimens were punched out and submitted for evaluation. Similarly prepared were coated aluminum foil specimens for enriched oxygen environmental flammability tests. Upon

impact-testing (10 Kg-m) in liquid oxygen, the same low level of contamination was obtained as described previously. Thus, 2/20 and 2/20 reactions were obtained using PFPOI which had previously yielded similar results when cured with UPFPOH.

The film preparation using 1210 mol. wt. PFPOI was repeated, and the sample set submitted to NASA-MSFC for test.

B. Melamine as a Curing Agent for PFPOI

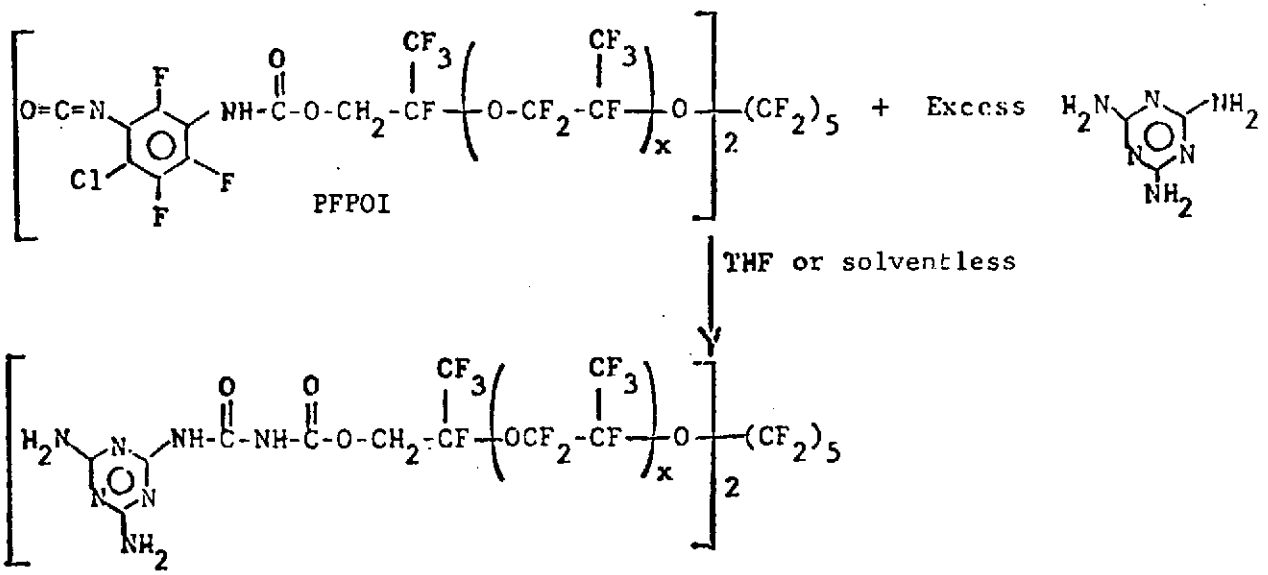
The search for a suitable curing agent, to produce more efficient and thermally stable crosslinks, was extended to include trifunctional derivatives of sym-1,3,5-triazine, known for their nonflammability characteristics.

1. Rationale

The rationale behind their use is quite similar to the case of cyano-guanidine above, namely, (1) the absence of potentially labile (oxidatively) carbon-hydrogen bonds; (2) attenuated reactivity of the functionality to allow incorporation into the polymer system with resultant satisfactory handling and processing parameters, such as pot-life and cure schedule; and (3) higher crosslink density, due to high functionality/molecular weight ratios, to concurrently provide a greater multiplicity of rigid ring structures at the extension/crosslink site. Such a condition would be expected to yield a greater degree of toughness and improvement in the elastomeric nature of the cured polymer.

2. Evaluation

Simple admixture of melamine with the PFPOI prepolymer was found to be unsuitable for producing cured material. Severe insolubility and infusibility restrictions precluded such incorporation, since the mixture remained heterogeneous even at temperatures up to the decomposition point of the PFPOI prepolymer (280°C). Cure of the system did occur at lower temperatures, but the marked heterogeneous appearance of the resin mixture suggested that the cure apparently proceeded through an allophanate mechanism.

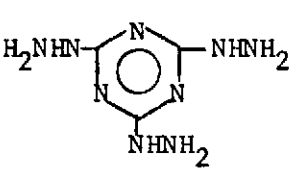


Attempted Melamine-capped Prepolymer Preparation

Attempts to "end-cap" the functionally-terminated PFPOI prepolymer with melamine in solvent (e.g., tetrahydrofuran) likewise proved unsatisfactory. The insoluble nature of melamine did not allow sufficient reagent to be present to effectively react with the isocyanate-terminated polyperfluoropropyleneoxide telomer.

Prolonged refluxing of the heterogeneous reaction mixture resulted in gel formation. Again the crosslink (gel) apparently formed through purely thermal allophanate formation. The essentially complete insolubility of melamine precludes its further investigation as a curing agent for PFPOI.

C. Cyanuric Trihydrazide as a Curing Agent for PFPOI

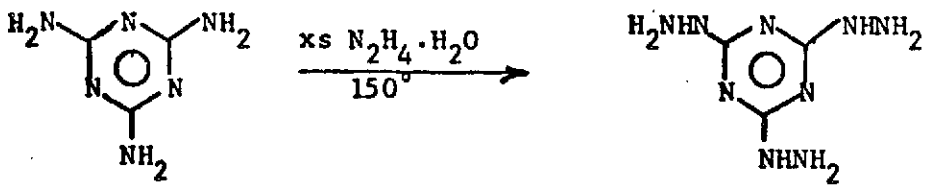


Cyanuric Trihydrazine

Following the rationale described above for melamine, attention was next directed to the use of the title material. It was expected that the enhanced reactivity of the hydrazide (as compared to the amide) functionality of this reagent would facilitate the desired cure reaction. Three separate attempts were made to synthesize cyanuric trihydrazide (2,4,5-trihydrazinotriazine) in high purity. The only available reference describing the preparation is quite old and relatively vauge.(1)

(1) R. Stolle and K. Krauch, Ber. 46, 2337 (1913).

The preparation has been carried out by reaction of melamine with hydrazine hydrate at 150°C for 5 hours.



Cyanuric trihydrazide

When this procedure was carried out, the only isolable product (i.e., recrystallizable from hot water) was a material which did not melt below 350°C (vs. lit. mp 287°C). This product appeared to oxidize rapidly with exposure to air. Infrared analysis was, however, consistent with the proposed structure.

Consequently a mixture of PFPOI and the assumed CTH was prepared and cured at 121°C overnight. The system gelled, without noticeable incorporation of the CTH into the polymer, as evidenced by the heterogeneous appearance of the glled specimen.

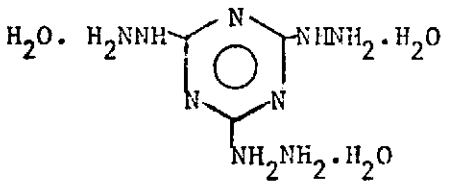
This synthesis was repeated with similar results.

Two attempts were made to prepare the desired CTH from cyanuric chloride and hydrazine in (1) dioxane and (2) n-butanol. In both instances, the cyanuric chloride was added as a solution in the specified solvent to a large excess of hydrazine in solution. After the exothermic addition, reflux was maintained overnight. The resulting slurries were extremely difficult to filter. A number of filtering devices was utilized with no improvement. Centrifugation, while time consuming, provide to be the best method. Repeated water washing followed by centrifuge treatment and decantation finally resulted in removal of all traces of chloride ion ($AgNO_3$ test). The white product (insoluble in boiling water) did not melt (at <350°C). Its reaction with PFPOI, as a curing agent, was essentially identical to that of the material isolated from the previous preparation procedure.

A sample of the above compound was received from Fairmount Chemical Company and initial studies were begun on evaluating its effectiveness as a curing agent for the diisocyanate-capped PFPOI prepolymer.

Differential thermal analysis (DTA) of the as-received material showed a broad endotherm between ~60 and 150°C (inverse peak at 115°C) followed by a large exotherm beginning at approximately 180°C, and a peak at ~265°C. Literature melting points are ambiguous for this material, with values reported of from a low of 283°C to a high of over 350°C. When a capillary melting point of the sample was taken, no melt was apparent below 360°C although some softening (or sintering) was discernable. Similarly no significant evolution of volatiles was visually apparent.

The infrared spectrum indicated some slight amount of adscrbed moisture. Hence, a sample of the very finely divided powder was dried at 65°C/10 mm for 6 hours. There was a total weight loss of 24% which is unreasonably high for absorbed moisture. Hence, discreet hydration of the three hydrazino groups cannot be ruled out, viz:



A DTA scan of the dried sample was markedly different from that of the initial as-received sample. No endothermic peak was apparent. In addition, the exotherm broadened (110°C to 280°C) and decreased in height considerably. Whether these observations are attributable to a dehydration phenomenon coupled with a decomposition to gaseous products has not yet been resolved, although the hypothesis seems reasonable in light of the experimental conditions.

Thermogravimetric analysis of partially dried (95°C) material showed a rapid loss in weight (8%, attributable to water loss), a plateau to 220°C with ensuing decomposition and rapid weight loss. Figure 1 shows the DTA and TGA scans obtained with this partially dried material.

Mixtures of PFPOI and trihydrazinotriazine (as received) were admixed (by milling), and the cure followed visually with peculiar results. With this "as received" material, gellation occurred in 20 minutes at 100°C. Unreacted material was visually apparent in the opaque white gelled material. In this case, gellation may have proceeded through a combination of hydrolysis of the isocyanate, with subsequent urea and biuret formation.

The course of cure was followed by observing the behavior of the system from 25°C to 260°C at a 10°C/min heat up rate. At no time was there indication of any significant solubility of the curing agent in the prepolymer PFPOI.

This study was repeated using thoroughly "dried" trihydrazinotriazine. Similar insolubility was encountered, with an increase in the gel time, from the previous twenty minutes to 60 minutes at 100°C observed. The most ready explanation for the decrease in gellation rate is to involve at least partial competition of residual water with the hydrazine functions for the available isocyanate groups. Thermogravimetric analysis of the mixture (dried curing agent/PFPOI) showed no weight loss (by decomposition of the triazine) up to the decomposition point of the polymer (280°C).

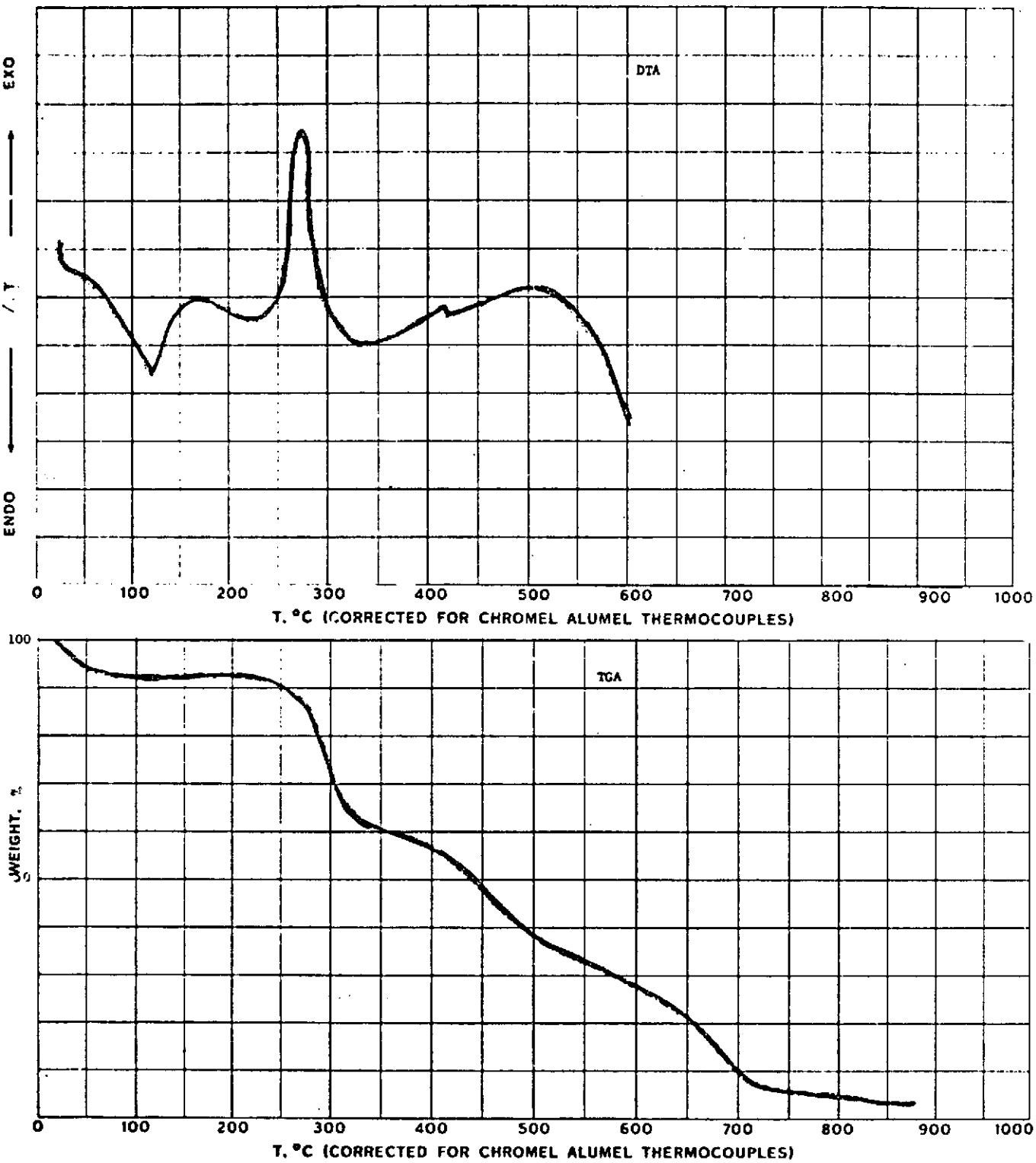


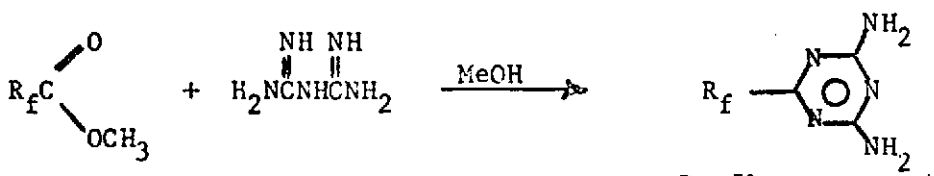
Figure 1. Thermograms of Partially-Dried Cyanuric Trihydrazide Sample

The use of cyanuric trihydrazide as a curing agent for PFPOI prepolymer was also consequently terminated.

D. Perfluoroalkylether Substituted Guanamines

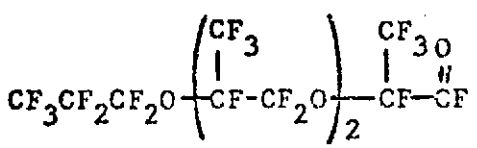
1. Derived from Mono-functional Acyl Fluorides

Substituted guanamines, of the type shown below, represent an interesting, alternative curing agent candidate.

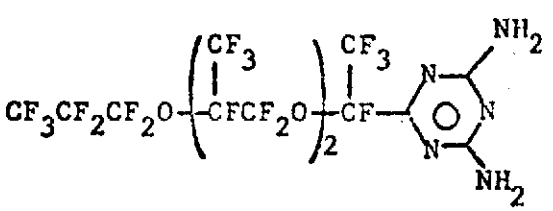


Perfluoroguanamine

Once again reduced reactivity of the amine functionality was expected to provide a reasonable reaction rate with the isocyanate. Improved solubility, flexibility and lower melting point was also expected, providing the perfluoroether (Rf) segment is of insufficiently high molecular weight. Toward these ends, a pure component was isolated from lower molecular fractions of the distillation of crude PFPOF, which has been tentatively identified as the following monofunctional acid fluoride.



Esterification of this material, followed by reaction with biguanide resulted in isolation of a waxy solid product, melting at 73°-75°C. The infrared spectrum was consistent with the proposed guanamine structure below.



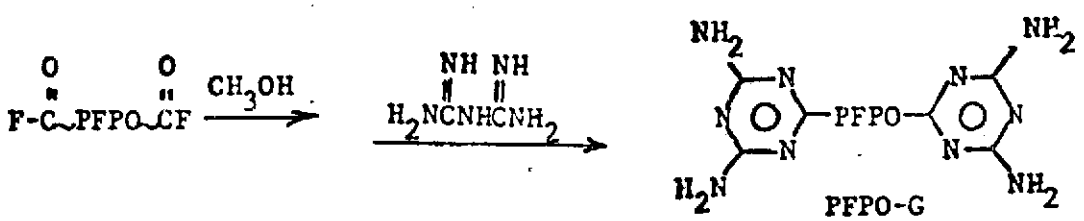
Molecular weight determination, by VPO in acetone, along with end group analysis, by perchloric acid titration in acetic acid, gave comparable results, with molecular weights of 732 and 690 respectively; vs. a theoretical molecular weight of 727.

These results obtained on the monofunctional guanamine-terminated perfluoropropylene oxide, demonstrate single protonation of the guanamine moiety in the perchloric acid titration.

All attempts to prepare a urea-extended biuret-crosslinked system using PFPOI and MFG resulted in a brittle fragile polymer which was considered unsuitable for the present application.

2. Bis-Guanamine Derivatives of Difunctional PFPO (PFPO-G)

Following a similar procedure, we have tentatively identified bis-guanamines (PFPO-G) prepared from an unfractionated homologous series of difunctional (acyl fluoride-terminated) polyperfluoropropylene oxide by reaction of the derived methyl ester with biguanide:



The rationale for the suitability of PFPO-G is based on a consideration of the multiplicity of amine-extension-cure sites (four), coupled with the total absence of oxidatively-labile carbon-hydrogen bonds. Use of such a system was expected to result in a superior cure and enhanced thermal capability for the derived polymer, inasmuch as all extension/crosslink bonds formed are urea linkages in a 1/1 NH_2/NCO ratio as in Figure 2. Such linkages are of known higher thermal stability than the normal urethane carbamate/allophanate crosslink.

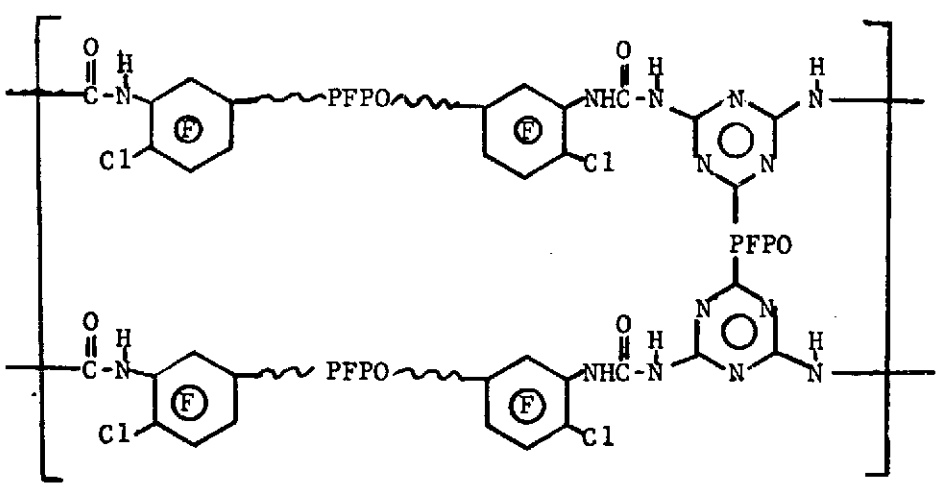


Figure 2. Idealized Extended/Cured Polyurea from PFPO-I/PFPO-G

The high density of rigid aromatic rings in this structure, coupled with the efficient hydrogen-bonding capability of the urea and urethane moieties was expected to produce a tougher system in fabrication.

The synthesis was carried out using PFPOF of 1360 average molecular weight. The conversion of the isolated methyl ester was not characterized but converted directly to the derived guanamine. VPO data on the guanamine moiety resulted in an apparent molecular weight of 1620. Initial studies incorporating PFPO-G as a curing agent for PFPOI were then initiated.

The isolated PFPO-G is sufficiently mobile at ~80°C to permit adequate mixing and de-aeration of the PFPOI/PFPO-G system. Adhesive bonds were then prepared following the usual procedure. The NCO/NH_2 ratio was varied from 0.8 to 1.2/1 using two different cure schedules. One schedule (Schedule A) utilized a three-hour cure at 121°C (Table III, and the second (Schedule B) used 68 hours at 72°C (Table IV). In both instances evidence of incompatibility (cloudy mixtures) was obtained. The heterogeneity was more pronounced with the 72°C cure, and this system (surprisingly) demonstrated superior 94°C tensile shear strengths. Bond strengths in both series, however, were lower than those obtained from the cyanoguanidine cure.

TABLE III

BIS-GUANAMINE-EXTENDED/CURED PFPOI*
Schedule A: 3-hour cure at 250°F

NCO/NH_2 Ratio	Lap-Shear Tensile Strength, N/cm^2 (psi) RT	94°C
0.8/1	1490 (2160)	655 (950)
0.9/1	1270 (1840)	530 (770)
1/1	1350 (1960)	510 (740)
1.1/1	1380 (2000)	627 (910)
1.2/1	993 (1440)	490 (710)

TABLE IV

BIS-GUANAMINE-EXTENDED/CURED PFPOI*
Schedule B: 68-hour cure at 160°F

NCO/NH_2 Ratio	Lap-Shear Tensile Strength, N/cm^2 (psi) RT	94°C
0.8/1	1660 (2410)	531 (770)
0.9/1	1680 (2440)	538 (780)
1/1	1710 (2480)	490 (710)
1.1/1	1670 (2420)	655 (950)
1.2/1	1730 (2510)	390 (565)

* Prepared from PFPOF of 1360 molecular weight.

The preparation of the guanamine-terminated PFPO-G was then repeated with inclusion of an additional step to insure complete removal of sodium chloride, which was utilized to break a water emulsion formed during the washing of the derived curing agent. Based on this additional washing, the previously-observed inhomogeneity of sample polymer prepared from PFPOI and PFPOG can now be ascribed to the presence of residual sodium chloride. Polymers recently prepared from these prepolymers, with the washing step, are colorless with essentially no evidence of waxiness.

An additional series of tensile shear bonds at varying NCO/NH_2 ratios were prepared, for comparative effectiveness evaluation. Surprisingly, the results indicate essentially the same non-varying response previously obtained with this system, throughout the range of NCO/NH_2 ratios employed. The cure schedule used in this study was 16 hours at 121°C and the results are summarized in Table V.

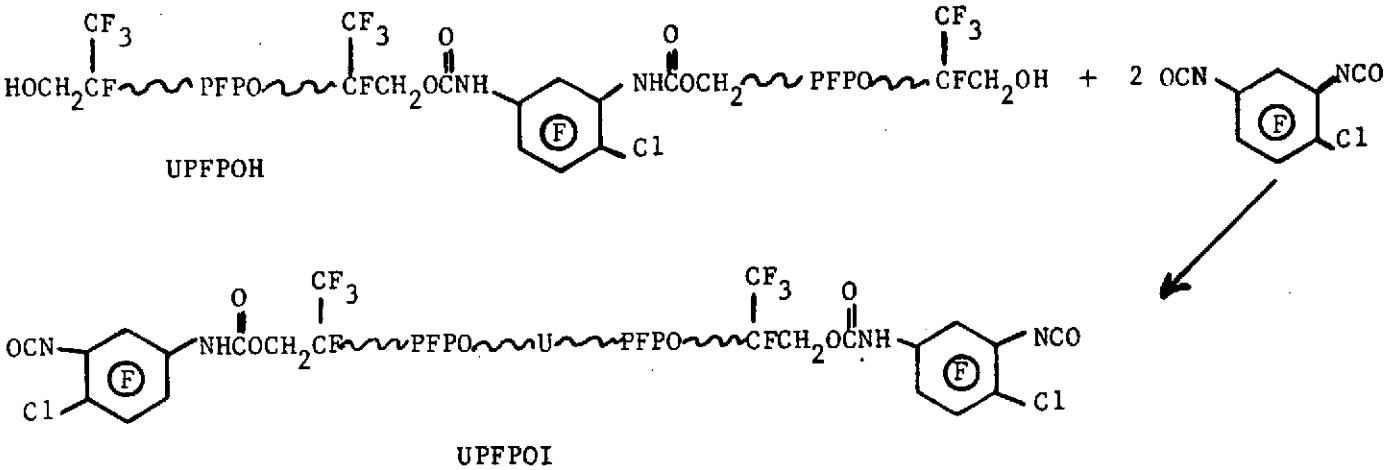
TABLE V

BIS-GUANAMINE UREA-EXTENDED/CURED
PFPOI-PFPO-G ADHESIVE PERFORMANCE
Schedule C: 16 hours at 121°C
1360 Mol. Wt. PFPOF

NCO/NH_2 Ratio	Lap-Shear Tensile Strength, N/cm^2 (psi)		
	-196°C	RT	94°C
1/1	1740 (2530)	1420 (2065)	434 (630)
1.15/1	1860 (2700)	1530 (2215)	531 (770)
1.3/1	1285 (1865)	1420 (2055)	364 (528)

3. Preparation of Various PFPOG Cured Polyurethanes from PFPOF of 1280 Mol. Wt.

Since it was apparent that the optimum crosslink density of the system had certainly not been realized, further extension through urethane formation was investigated to improve the properties. Toward this end a series of prepolymers was prepared, based on PFPOF of 1280 molecular weight yielding in turn PFPOG, PFPOH and PFPOI of 1400, 1250 and 1750 molecular weight, respectively. Then a urethane-extended, isocyanate-terminated prepolymer (UPFPOI) was prepared by the following reaction:



UPFPOH

UPFPOI

Reaction of this prepolymer (3250 mol. wt.) with PFPO-G (1400 avg mol. wt.) with a 1/1 NCO/NH_2 ratio, using two separate cure schedules, gave the following tensile shear adhesive strengths (Table VI).

TABLE VI

UPFPOI CURED WITH PFPOG (NCO/NH_2 = 1/1)

	Tensile Shear Strength, N/cm^2 (psi)		
	-196°C	RT	94°C
A	945 (1370)	1320 (1910)	200 (290)
B	1085 (1575)	1300 (1890)	340 (490)

NOTE: A - cured 18 hr at 82°C
B - cured 18 hr at 82°C plus 2 hr at 121°C

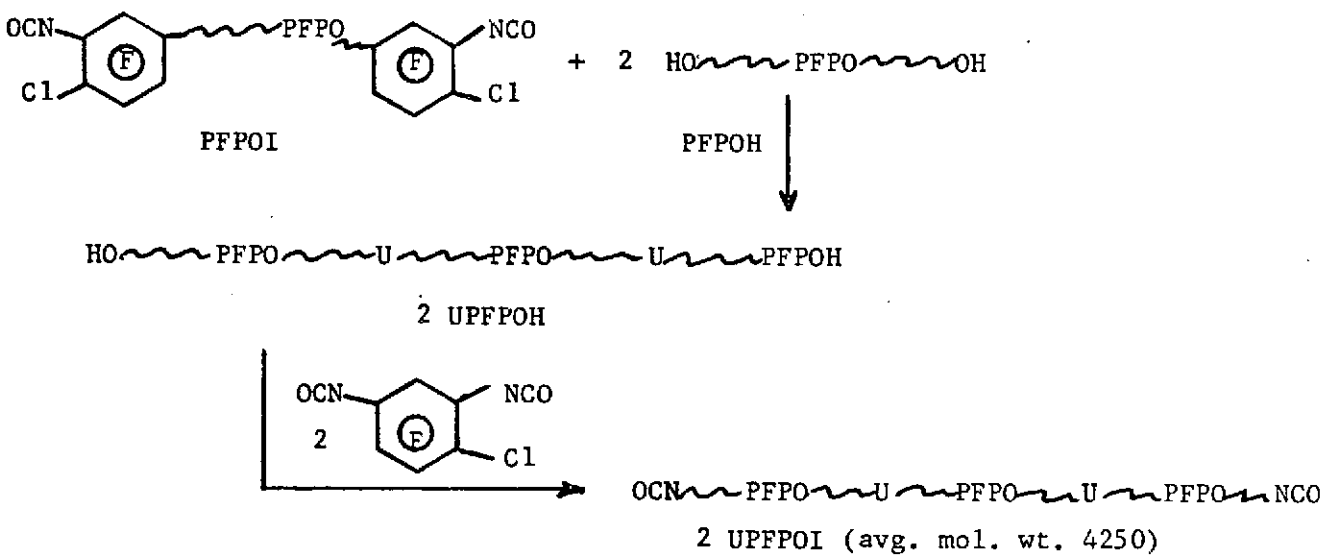
Next, formulations were compounded using, in C, below, an equimolar mixture of UPFPOI and PFPOI (to yield an overall avg. mol. wt. 2500) and in D, a 1/3 molar ratio of same (overall avg. mol. wt. 2120). Reaction with PFPOG, using the cure schedule in A above, yielded the following results:

	-196°C	RT	94°C
C	840 (1220)	1320 (1920)	245 (355)
D	1000 (1450)	1300 (1880)	200 (292)

To evaluate the effect of adventitious moisture on cured polymer properties formulation as in D was repeated (D'), and the cure (Schedule B) was carried out under a dry nitrogen atmosphere. The results were essentially the same as previously determined in an ambient environment.

	-196°C	RT	94°C
D'	1000 (1445)	1180 (1710)	160 (230)

To further check the "end-group" distance effect, a third isocyanate-terminated prepolymer was prepared which we designated 2UPFPOI, by the following sequence:



A previously reported, these preparations were carried out using infrared spectroscopy to monitor the relative changes in O-H and N-H stretch bands.

With three urethane extended isocyanate-terminated prepolymers of different molecular weights [1750 (PFPOI), 3250 (UPFPOI) and 4750 (2UPFPOI)] in hand, a series of copolymers were prepared using PFPO-G of 1400 molecular weight with each of the candidates. Varying molar ratios of the three were used, at a 1/1 NCO/NH_2 stoichiometry. Cure in all cases was 24 hours at 121°C. Results are tabulated in Table VII.

TABLE VII

EFFECT OF AVERAGE MOLECULAR WEIGHT OF ISOCYANATE TERMINATED PREPOLYMER ON PFPO-G CURED SYSTEM

Polymer No.	Molar Ratio of Prepolymers			Avg. Mol. Wt. of Prepolymer	Tensile Shear Strength, N/cm^2 (psi)		
	PFPOI	UPFPOI	2UPFPOI		-196°C	RT	94°C
E	1	--	--	1750	1230 (1790)	1720 (2500)	620 (900)
F	3	1	--	2130	710 (1030)	1100 (1600)	255 (370)
G	2	2	--	2500	760 (1100)	1370 (1990)	300 (430)
H	1	3	--	2830	650 (940)	1080 (1570)	220 (320)
I	--	1	--	3250	430 (620)	950 (1380)	20 (30)
J	--	3	1	3615	370 (540)	920 (1340)	14 (20)
K	--	2	2	4000	320 (470)	850 (1230)	14 (20)
L	--	1	3	4375	930 (1350)	1130 (1640)	62 (90)
M	--	--	1	4750	1030 (1500)	1190 (1730)	110 (160)

These results show a gradually decreasing trend with increasing molecular weight in lap-shear strength values at all temperatures tested. The same brittle character of the adhesive with a corresponding lack of toughness was prevalent with these systems, similar to that described above.

The lack of toughness demonstrated by this derived ternary system was unanticipated. It was felt that this strength deficiency could be most efficiently surmounted by a simple extension in the molecular weight of the starting acid fluoride-terminated, PFPOF, prepolymer system. Toward this end, the entire series of intermediate prepolymers, coded PFPOF, PFPOH, PFPOMe, PFPOG and UPFPOH, was synthesized in higher molecular weight with significant results. The molecular weight of the starting PFPOF was determined to be 1555, vs. MW = 1280 for prepolymer utilized in previous work.

A description of the various syntheses involved in the terpolymer is outlined in a subsequent section of the report. Preparation of the PFPOI, UPFPOH and PFPOG derivatives was successfully accomplished with corresponding increases in the molecular weight of all species.

In all cases good correlation of analytical data was obtained. For the complete characterization of the bis-guanamine-terminated PFPO-G curing agent, recourse was made to volumetric analytical techniques.

The synthesis of this system, derived from higher molecular weight acid fluoride-terminated perfluoropropylene oxide, PFPOF, MW = 1555, was obtained with complete guanamine termination. The molecular weight (by VPO in acetone) was established as 1711, vs. a theoretical molecular weight of 1682. End group analysis (perchloride acid titration in acetic acid) yielded an equivalent weight of 816, which agrees well for the theoretical structure with a singly protonated guanamine moiety, which was previously determined to be the case with the mono-substituted guanamine case described above.

4. Preparation of Various PFPOG (Guanamine-Terminated Perfluoropropyleneoxide)-Cured Polyurethanes from Higher Molecular Weight PFPOF

With the successful preparation of the three requisite prepolymers, a) the isocyanate-terminated perfluoropolypropyleneoxide, PFPOI; b) the reverse hydroxyl-terminated perfluoropolypropyleneoxide, UPFPOH; and, c) the guanamine-terminated perfluoropolypropyleneoxide, PFPOG, all derived from higher molecular weight difunctional acid fluoride-terminated perfluoropolypropyleneoxide, PFPOF, studies were initiated on determination of cure schedules and stoichiometric variation in the derived fluorinated polyurethane systems.

Initial experiments using stoichiometric equivalencies of PFPOG (assuming tetrafunctionality) and PFPOI produced minor improvements in toughness of the resultant cured elastomer system, with essentially the same low tear resistance. It had been anticipated that significant improvement in this latter parameter would be obtained, by the use of the higher molecular weight prepolymers.

An evaluation was then carried out regarding the effect of incorporating quantities of the urethane-extended hydroxyl-terminated perfluoropropyleneoxide, UPFPOH, as a partial molar substitute for the guanamine-terminated perfluoropolypropyleneoxide, PFPOG, curing agent. All modifications were carried out using strict stoichiometric ratios. In other words difunctionality of the hydroxyl-terminated prepolymer UPFPOH and tetrafunctionality of the guanamine-terminated prepolymer, PFPOG, were assumed. Marked improvement in cured resin toughness and overall elastomeric character was obtained for the derived resin systems containing mole percentages of UPFPOH of 60-80%. The elastomer samples exhibited a rapid recovery following elongation. The tear strength was also much improved.

Cure of the systems was monitored by infrared spectroscopy, which demonstrated complete cure in a stannous octoate (0.5% based on total polyether)-catalyzed system at 121°C.

Toughness and elastomeric character was also greatly enhanced at elevated (cure) temperature. This study has provided the first demonstration on this entire program of truly elastomeric character for a cured resin system based on perfluoropolypropyleneoxide.

Two comparison series of castings and films were prepared using both dry nitrogen and ambient air atmospheres. The purpose of this comparison was to determine whether any significant differences in final properties would be achieved due to the exposure to reactive atmospheric moisture. The cure was followed by hardness measurement (room temperature) following various cure intervals at 121°C. The changes in hardness and qualitative observations of the bulk character of the cured resin castings are tabulated below in Figure 3.

After the complete 4 hour cure no significant difference was noted between the cures in nitrogen and in air. Toughness and flexibility of the castings appeared equivalent for the two environments, and in all cases was quite acceptable.

These results appeared to be quite promising. Consequently, a series of tensile shear- and "T"-peel-specimens was prepared with the expectation of significantly improved adhesive bond strengths. The results are tabulated in Table VIII as a function of mole-percentage of the guanamine-terminated perfluoropolypropyleneoxide, PFPOG, component.

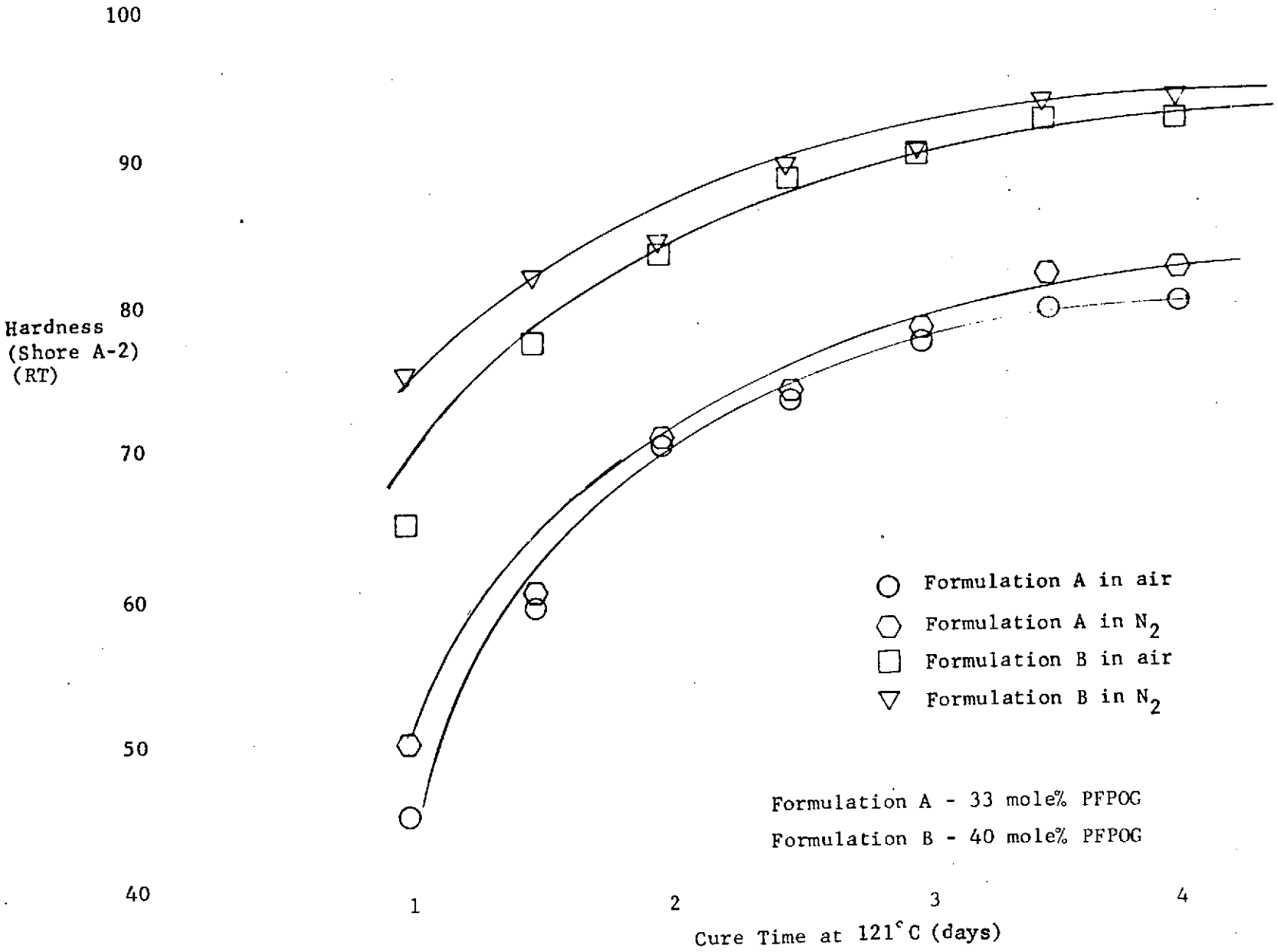


Figure 3. Effect of Cure Time on Resin Hardness

TABLE VIII

ADHESIVE PERFORMANCE OF PFPOI/UPFPOH/PFPOG TERPOLYMER SYSTEMS

Mole % PFPOG	Lap Shear Tensile Strength at Temperature N/cm^2 (psi)			Peel Strength at Room Temperature N/cm^2 (p.i.w.)
	-196°C	RT	94°C	
40	420 (615)	550 (800)	44 (64)	2.1 (1.2)
33	410 (590)	440 (640)	33 (48)	0.9 (0.5)
15	275 (400)	170 (250)	12 (17)	

All the specimens tested displayed ca. 100% adhesive failure. The low performance levels were initially attributed to incompletely (or improperly) etched adherend surfaces and the experiments repeated (and augmented) with freshly prepared sodium dichromate/sulfuric acid etchant solutions.

Results were again disappointing with the same failure mode, i.e., entirely adhesive failure as shown in Table IX. These results are essentially of the same magnitude as those previously obtained, and clearly show that these low properties are not due to improper metal preparation.

TABLE IX

REPEAT ADHESIVE PERFORMANCE OF PFPOI/UPFPOH/PFPOG TERPOLYMER

Mole% PFPOG	Lap Shear Tensile Strength at Temperature N/cm^2 (psi)		
	-196°C	RT	94°C
33	550 (795)	480 (700)	65 (95)
37.5	670 (975)	510 (740)	46 (67)
40	500 (728)	655 (950)	84 (122)
42.5	655 (950)	600 (870)	60 (81)
48	490 (715)	590 (855)	80 (115)
56	590 (850)	660 (960)	76 (110)

Only preliminary conclusions may be drawn from these results. The marked change in properties of the more extended terpolymers, from hard plastic materials to true elastomers is indeed most promising. This improvement may be attributable to a number of contributory factors. The inherent flexibility of the PFPO chain appears to be significantly affecting the bulk resin properties. This obvious improvement in flexibility (and elasticity) has not, however, produced a corresponding improvement in adhesive lap-shear tensile performance. This may be due to a significant decrease in the overall concentration of polar "bonding" groups, with the system consequently assuming a more fluorocarbon-like nature.

It was anticipated that utilization of a metal primer would improve the adhesion and allow translation of the superior bulk resin properties to the adhesive application. Toward this end a series of tensile shear specimens were prepared, using commercially-available primer systems. Those primers utilized, while representing only a cursory sampling of potential candidates, nevertheless represented sufficient diversity of functionality to allow a reliable estimation of the potential applicability of primers in general. This assumption is predicated on adequate wetting of the primed metal substrate by the applied adhesive.

As can be seen from the results tabulated in Table X, these anticipations have not been realized.

TABLE X

TENSILE SHEAR STRENGTHS OF PRIMED ADHERENDS

Primer System	Type	Avg Tensile Shear Values, N/cm^2 (psi)		
		-196°C	RT	94°C
Unprimed metal	--	400 (580)	680 (980)	83 (120)
A-1100	Amino siloxane	92 (133)	430 (620)	14 (20)
Z-6040	Epoxy siloxane	365 (530)	910 (1320)	83 (120)

The adhesive mixture consisted of 60/40 (NH_2/OH) mixture of PFPOG/UPFPOH in stoichiometric balance with PFPOI. Again the failures were essentially completely adhesive in nature.

5. Bulk Resin Properties of the Ternary PFPOG/UPFPOH/PFPOI

Micro-tensile "dog-bones" specimens were cut from cast specimens of the various formulations of the ternary polymer system. The specimens were cast in a standardized manner by pouring the mixed resin into a mold, de-gassing at ~75°C, then curing for 4 hr at 121°C in air. Careful control of stoichiometry was maintained between isocyanate content and active hydrogen (-OH and $-NH_2$) termini. Results are shown in Table XI below.

TABLE XI

TERNARY RESIN SYSTEMS BULK PROPERTIES

Mole Ratio NH_2/OH	Hardness Shore A-2	Tensile Strength N/cm^2 (psi) RT	Tensile Strength N/cm^2 (psi) 94°C	Tensile Modulus N/cm^2 (psi) RT	Tensile Modulus N/cm^2 (psi) 94°C	% Elongation at Break RT	% Elongation at Break 94°C
70/30	86	1370 (1990)	140 (200)	21,400 (31,000)	--	165	630
60/40	82	1300 (1880)	96 (140)	11,700 (17,000)	--	220	400
55/45	76	1250 (1820)	76 (110)	10,300 (15,000)	--	280	530

The physical properties of these various terpolymers show the expected changes, with respect to increases in hardness, modulus and tensile strength, with increasing amine content with corresponding decreases in elongation. These changes are readily attributable to crosslink density, and to urea content, generated through the tetrafunctional PFPOG component.

The properties obtained under ambient conditions are quite acceptable, matching several commercially-available polyurethane elastomer systems which are widely used in aerospace applications. It is felt that these properties should be adequate for many potential usages in applications where "polyurethane" performance in enriched oxygen environments is needed.

Difficulty has been encountered in obtaining acceptable adhesive performance at elevated temperatures. The bisguanamine (PFPOG) system does not appear to offer the improvements anticipated, based on its structural advantages. It may eventually be determined that the most important value of the PFPOG prepolymers lies in inclusion into other ternary systems where it may be used as a co-curing agent with low molecular weight multifunctional nonflammable functionally-terminated prepolymers which are capable of providing "tighter" crosslinks.

PHASE I
CONCLUSIONS

The results of work conducted to date on this program may be summarized as follows:

I. STRUCTURAL ADHESIVE FORMULATIONS

A. Allophanate Cured System (PFPOI and UPFPOH)

Lap shear tensile strength levels have been found to be highly reproducible and consistent, with values of from 3500-5000 N/cm^2 obtained at cryogenic (-196°C) temperatures, along with values of ca. 1500 N/cm^2 at ambient temperature. Moderately elevated temperature (>66°C) performance still remains deficient, with only slight improvement obtained over previous PFPO systems (200-350 N/cm^2 at 94°C) investigated. This deficiency is of course related to the thermally-reversible allophanate cure mechanism itself. Improvements are treated below.

Liquid- and gaseous-oxygen impact compatibility has been demonstrated at pressures up to 1035 N/cm^2. To WRD's knowledge this PFPO resin system is the only workable adhesive existent which possesses these outstanding oxidation resistant characteristics.

B. Improved High Temperature Performance

Significant improvements in overall performance has been obtained by the utilization of alternate nonflammable curing agents. The most promising system, to date, involves the incorporation of either cyanoguanidine or the bis-guanamine-terminated perfluoropropyleneoxide telomer (PFPO-G) as extension-curing agents for the isocyanate-terminated PFPOI system. Lap shear tensile strength values in excess of 700 N/cm^2 at 94°C have been obtained using these modified systems.

Significant improvements in elastomeric character with the PFPO system have been achieved by use of the PFPO-G-tetrafunctional (amine) curing agent combination. A truly elastomeric material at temperatures up to 121°C has been synthesized. These same improvements in elastomeric nature have not, however, been translated into corresponding improvement in adhesive values. This lack of improvement in adhesion with the higher molecular weight resin has been preliminarily ascribed to the effect of the increased fluorocarbon (nonbonding) content of the overall elastomer system.

Synthesis or utilization of a suitable primer is expected to result in upgraded adhesive performance of this elastomer.

Other nonflammable curing agents investigated on this program include melamine and cyanuric trihydrazide. Both of these initially attractive candidates were found to be ineffective in the desired application, largely due to insolubility problems, and future use is considered impractical.

PHASE II

RELIABILITY AND WELD-BOND STUDIES

PHASE II
INTRODUCTION AND OBJECTIVES

The efforts of this phase were directed toward accomplishing a two-fold purpose. First, to establish reproducibility and reliability in the PFPOI/UPFPOH fluorinated urethane system in both adhesive and liquid oxygen compatibility characteristics. Secondly, to determine the feasibility and investigate the necessary adjustments in formulation to provide an adhesive which would be suitable for use in a "weld-bond" configuration in liquid oxygen tankage for advanced space-flight vehicles.

PHASE II
TECHNICAL DISCUSSION

I - PFPOI/UPFPOH POLYURETHANE SYSTEM

A. Preliminary Preparations of PFPOI/UPFPOH Polyurethane System (Batches 1, 2, and 3)

Synthesis of the basic polymer system was initially carried out three consecutive times with the aim of establishing reliability in liquid oxygen and high pressure gaseous oxygen.

Materials acquisition, solvent repurification for the repeat syntheses and preliminary preparation of perfluoroglutaryl fluoride was completed early. Each step of the preparation requires strict adherence to already established procedures which, in turn, contain rigorous cleaniness procedures, inspections, and precautions against contaminants. If an unexpected reaction (in oxygen) occurred then the entire procedure was to be reviewed and repeated with suitable modification until three separate consecutive preparations will have been proven to be compatible.

The preparations have been described previously (cf. Phase I).

The isolated diacylfluoride-terminated PFPOF from Step 2 in the various syntheses was deliberately fractionated so that variations in overall average molecular weight would result.

Analytical data exhibited the expected good correlation between the three measurement modes; vapor pressure osmometry, vapor phase chromatography and end group analysis.

	Molecular Weight by			
PFPOF from	VPO	VPC	EGA(x2)	b.p. (°C/torr)
Prep. 1	1427	1450	1474	115-190°/0.05-0.1
Prep. 2	--	1135	1120	95-168°/0.02
Prep. 3	--	1386	1412	106-157°/0.02-0.03

Reduction, (lithium aluminum hydride) followed by purification by low pressure distillation yielded the desired PFPOH hydroxyl terminated material with the boiling ranges shown below.

PFPOH from	b.p. Range (°C/torr)
Prep. 1	156-174°/0.2-0.1
Prep. 2	150-168°/0.5-0.8
Prep. 3	144-154°/0.1-0.08

Conversion of the PFPOH to the corresponding urethane extended hydroxy-terminated UPFPOH, as well as to the isocyanate-terminated PFPOI by reaction with 4-chloro-1,3,5-trifluoro-m-phenylene diisocyanate proceeded normally. The time for completion of the PFPOI preparation was 3-4 hours at 108°-110°C.

B. Preparation of Bonds and Film Samples

Tensile shear bonds were prepared in the usual fashion using dichromate/sulfuric acid etched clad 2024-T6 adherends. Normal 1.8/1 overall NCO/OH ratio was maintained by mixing the two prepolymers PFPOI/UPFPOH at a 13/1 mole ratio. Cure was 82°C for 4 days (0.004 in. glueline thickness). Results of initial tests on Batch 3 are listed below.

Lap Shear Strength N/cm^2 (psi)		
-196°C	RT	94°C
3380 (4900)	1490 (2160)	217 (315)

A second series of bonds from the same batch of PFPOH (thru the PFPOI and UPFPOH precursor) was prepared and the results indicate essential duplication.

Lap Shear Strength N/cm^2 (psi)		
-196°C	RT	94°C
4030 (5850)	1480 (2140)	440 (635)

Two sets of film samples (~0.010 in.) were simultaneously cast and cured for all three individual preparations. One of these was cast on GS-3 fluorocarbon released aluminum while a second was cast on solvent (trichlor) cleaned Teflon. Compatibility specimens (11/16 in. diameter) were punched from each cured film. Careful handling is very critical during this step. Close inspection of the individual specimens under ~40 power magnification often reveals spurious contamination with dust particles. A sample exhibiting such contaminants is discarded.

The allowable tolerance (i.e., the level of tolerable contaminant) is undefined and in fact may never by precisely determined. It is to be surmised that the particulate contamination [even though it is not impact sensitive (oxygen) in itself] creates very high energy loading level on a microscopic level which initiates spurious reaction in oxygen rich environments. The inspected samples were then submitted to MSFC for testing.

C. Liquid Oxygen Compatibility Testing of Batches 1, 2 and 3

These samples (which were prepared from three separate complete syntheses above) all showed the same low level sensitivity (i.e., one or two reactions per 20 sample set at 10 kg-m impact loading).

The procedures followed in these preparations were those previously developed wherein the material was shown to be batchwise compatible with both liquid and gaseous oxygen at both atmospheric (10.3 N/cm^2) and high pressures (1035 N/cm^2).

The repeated low-level sensitivity was initially attributed to contamination of the specimens during cure or in postcure handling operations. Very close inspection (under low power magnification) has demonstrated the presence of foreign particulate contaminants at a low level of occurence (e.g., approximately 1 of every 4 11/16 in. diameter disc samples is discarded for this reason). The particulate material (dust) is inadvertently introduced during the mixing and casting operations since the particles are almost invariably embedded in the cured resin.

An alternate source of sensitivity may possibly lie in the low pressure distillation steps employed during isolation of the various prepolymer preparations. Silicone stopcock grease has been utilized routinely for these operations. Extremely small amounts of this medium may possibly be incorporated in the as-recovered products and carried through to final polymer preparation.

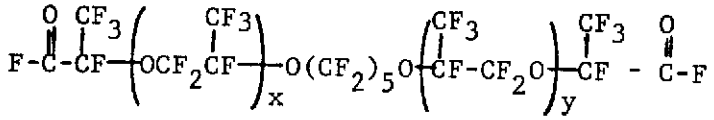
D. Preparation of Batches 4, 5, and 6 of PFPOI/UPFPOH Polyurethane

We had planned to begin additive and weldability studies during the earlier part of this phase. However, our plans were drastically altered following receipt of the preliminary LOX impact tests.

As a consequence of these results, we promptly began another series of preparations.

A significant change in synthetic technique was in substitution of Fluorolube lubricant for the standard silicone vacuum grease in all ground glass joints required during the various steps (reaction vessels, distillation apparatus, etc.). The prepolymer mixing and casting operations were carried out in "dust-free" glove-boxes and cure accomplished under aluminum covers.

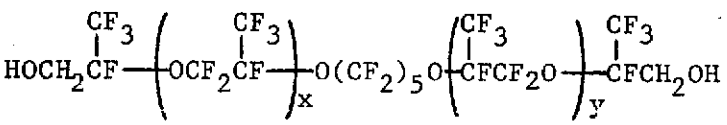
The syntheses showed no abnormal characteristics. Very good reproducibility in the acyl fluoride terminated difunctional PFPOF preparation is apparent from the following table.



PFPOF

Batch Number	b.p. °C/Torr	Molecular Weight EGA	VPC
4	97-136/0.02-0.10	1410 ±40	1390
5	95-141/0.04-0.10	1414 ±24	1383
6	85-133/0.04-0.05	1340 ±40	1332

Reduction (lithium aluminum hydride) was carried out on the isolated PFPOF from Batches #4, #5 and #6 to yield the corresponding difunctional hydroxyl terminated PFPOH.



PFPOH

Batch Number	b.p. °C/Torr
4	158-174/0.5-0.7
5	133-167/0.05-0.004
6	125-157/0.10-0.12

The precursor 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate was similarly redistilled using Fluorolube as stopcock lubricant. VPC analysis indicates 99.1% purity with the impurity tentatively identified as the fluorinated analog, 2,4,5,6-tetrafluoro-m-phenylene diisocyanate.

Preparation of the derived prepolymers PFPOI (isocyanate terminated) and UPFPOH (urethane extended hydroxyl terminated) by reaction with 4-chloro-1,3,5-trifluoro-m-phenylene diisocyanate proceeded with no unusual observations.

As previously mentioned, all syntheses have been carried out under scrupulously clean conditions. All glassware utilized has been cleaned with acetone, thoroughly rinsed, soaked in Chromerge overnight, thoroughly rinsed with distilled water, rinsed three times with trichloroethylene and blown dry with dry N2. Equally stringent conditions prevail in the

mixing, de-aeration, casting and curing procedures. All operations were carried out in either a polyethylene dry bag or (in the case of transfer or curing operations) in receptables suitably covered and sealed with aluminum foil.

E. Impact Sensitivity Testing of Batches 4, 5 and 6

These revised procedures resulted in improvement to very near the desired level of compatibility. Batch No. 4 (Coded 297-82B, 83B, and 84B) yielded the following results when tested in liquid oxygen at 10 kilogram-meter impact. The rejected specimens, which are those which had visible particulate contamination under low power magnification, were similarly tested (Table XII).

TABLE XII

LIQUID OXYGEN TESTING OF BATCH 4 PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT

Code	Reaction/Number of Specimens
82B*	2/20
82B rejects*	3/20
83B**	0/20
83B rejects**	0/9
84B**	0/20
84B rejects**	2/20

* Cast on Teflon sheet
** Cast on GS-3 fluorocarbon released aluminum

These results are confusing at first glance. It is difficult to imagine Teflon as imparting an incompatibility to the curing polyurethane. However, it must be borne in mind that a major variable in the compatibility test involves the specimen thickness. As the specimen thickness decreases, the sensitivity generally increases quite rapidly. In qualitative terms the compatibility test generates an essentially instantaneous adiabatic compression condition upon impingement of the plummet. Hence, a thicker specimen is more able to absorb this sudden excessively high energy loading and may well pass the test whereas a thinner specimen will react and fail.

A second, although more or less uniform, condition lies in the rebound impact of the dropping hammer. The initial impact at liquid oxygen temperature (-196°C) shatters (or at best, smears) the specimen to a much thinner dimension (hence, more sensitive). Rebound reactions are considered as failures.

Considerable variation in the nominal 9 mil thickness of the submitted specimens is more likely when Teflon sheet ($\sim$ 0.250 in.) is used as the substrate as compared to the surface ground aluminum plate.

Batch No. 5 was submitted as a series of 11/16 in. diameter discs in the following fashion, with the indicated results (Table XIII). The first number under results is the number of primary impact reactions; the second is the number of secondary rebound reactions; and the third the total number of specimens tested.

TABLE XIII

LIQUID OXYGEN TESTING OF BATCH 5 PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT

Code		Results
297-93A	cast on Teflon (0.006-0.009 in. thickness)	2/4/20
297-93A	rejects	0/0/10
297-93A	rejects rinsed with trichloroethylene	1/3/11
297-93C	cast on GS-3 released aluminum (0.008-0.009 in. thickness)	0/0/20
297-93C	rejects	1/1/12
297-93C	rejects rinsed with trichloroethylene	0/0/12

Whittaker Research and Development Division personnel witnessed the testing of 297-93C as part of a general conference at Marshall Space Flight Center. No reactions of the 20 specimen set were observed at 10 kg-m impact loading in liquid oxygen. Examination of the tested specimens revealed that sample disintegration to very small grains had occurred during the test. Whether disintegration occurs on the initial strike or during subsequent rebound impacts was not determinable.

Batch No. 6 (labelled 97-A and 97-C) was submitted after visual inspection for particulate contamination and was divided into three categories:

1. No particulate matter visible under low power magnification
2. Rejected specimens as is
3. Rejected specimens washed with trichloroethylene.

An apparent mixup in sample labelling occurred in this series. 97-A was cast on Teflon while 97-C was cast on aluminum which was released with GS-3 fluorocarbon. The rejected samples (both washed with trichloroethylene and as is) were inadvertently labelled incorrectly. The results are shown in Table XIV.

TABLE XIV

LIQUID OXYGEN TESTING OF BATCH 6 PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT

Sample	Results
97A*	3/5/60
97C* rejects	0/5/20
97C* rejects washed with trichloroethylene	0/1/20
97C**	1/1/60
97A** rejects	0/0/15
97A** rejects washed with trichloroethylene	0/2/15

* Cast on Teflon
** Cast on GS-3 released aluminum

F. Preparation and Liquid Oxygen Compatibility Testing of Batches 7, 8 and 9

Batch #7 labelled 329-7 was cast on GS-3 released aluminum, measured, and submitted in graded thicknesses. No inspection of washing was carried out. The results are shown in Table XV below.

TABLE XV

LIQUID OXYGEN TESTING OF BATCH 7 PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT

Thickness	Results
0.009-0.010 in.	0/0/20
0.008-0.009 in.	0/2/20
0.007-0.008 in.	0/0/20
0.006-0.007 in.	0/2/20

These results, which seem to provide good evidence against the necessity of the tedious visual inspection, again demonstrate the rebound impact reactions which were mentioned previously. The pulverization of the polymer to very small particle size on the initial impact presents a very serious problem when judging the efficacy of the test.

Batch #8 (labelled 329-14) was cast in five thicknesses on GS-3 released aluminum. The punched out specimens were rinsed in trichloroethylene after thickness measurements. No rejections for foreign particulate material was made. A total of 329 specimens were submitted in the following thicknesses with results as listed in Table XVI.

TABLE XVI

LIQUID OXYGEN TESTING OF BATCH 8
PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT

Thickness	Results
0.003-0.004 in.	0/2/60
0.004-0.005 in.	1/3/60
0.005-0.006 in.	0/1/60
0.006-0.007 in.	0/3/60
0.007-0.008 in.	0/0/8
0.008-0.009 in.	1/8/60

No real pattern in impact sensitivity with thickness is apparent. The most salient feature is that only 2 primary impact detonations were observed in the total of 308 specimens tested. This essentially insensitivity to thickness was not anticipated and is quite encouraging.

Batch 9 yielded the following results when tested under various liquid oxygen pressures at 10 kg-m impact (Table XVII).

TABLE XVII

LIQUID OXYGEN TESTING OF BATCH 9 PFPOI/UPFPOH POLYURETHANE AT 10 kg-m IMPACT UNDER VARIOUS LIQUID OXYGEN PRESSURES

Thickness	LOX Pressure (psi)	Results
0.007-0.008 in.	Ambient	1/3/40
0.007-0.008 in.	100	40/40/40
0.007-0.008 in.	500	20/20/20
0.008-0.009 in.	Ambient	2/5/40
0.008-0.009 in.	100	40/40/40
0.008-0.009 in.	500	40/40/40
0.008-0.009 in.	Ambient	0/0/40

These results demonstrate that the low level sensitivity found at ambient LOX pressure is translated to complete incompatibility in high pressure oxygen environments. These results were unanticipated and the root cause is still undetermined.

G. Bond Strengths

Tensile shear strengths of the PFPOI/UPFPOH systems have shown a surprising decrease in strength as refinements in purification and processing procedures have been upgraded. The liquid oxygen compatibility of some of the earlier batches was insufficient (1 to 3 failures/20 specimen sets) while good bond strengths were obtained.

For example, representative bond strength in those less compatible batches were found to be nominally 3500 to 5000 N/cm^2 at -196°C, 1400 to 1800 at RT, and 200 to 350 at 94°C.

The results (averages) from the last few batches which show acceptable compatibility are shown in Table XVIII.

TABLE XVIII

TENSILE SHEAR STRENGTHS OF PFPOI/UPFPOH

Batch No.	Tensile Lap Shear Strength, N/cm^2 (psi) -196°C	RT	94°C
5 (297-93)	2560 (3710)	900 (1300)	190 (270)
6 (297-97)	2140 (3100)	990 (1440)	270 (390)
7 (329-7)	2590 (3760)	1080 (1570)	100 (150)
8 (329-14)	2700 (3910)	990 (1440)	190 (280)

All the failed specimens show an adhesive failure mode. These results were unexpected and studies were run to determine the adhesive characteristics of such variables as NCO/OH ratio, cure schedule and effect of glueline thickness.

Tensile shear strength is apparently independent of glueline thickness (up to 0.005 in.) with the low modulus PFPOI/UPFPOH system. These results which were anticipated are listed in Table XIX.

TABLE XIX

EFFECT OF GLUELINE THICKNESS ON LAP SHEAR STRENGTH OF PFPOI/UPFPOH POLYURETHANE ADHESIVE (NCO/OH Ratio 1.8/1)

Glueline Thickness, in.	Lap Shear Strength, N/cm^2 (psi) (Avg of 6) -196°C	RT	94°C
<0.001	3180 (4610)	1340 (1950)	106 (154)
0.003	2640 (3830)	1410 (2040)	148 (214)
0.005	2640 (3830)	1320 (1910)	113 (164)
0.010	2430 (3530)	1160 (1680)	162 (235)

The failure mode was again adhesive in nature at all temperatures.

NCO/OH ratio adjustment yielded the following results (Table XX) at a nominal 0.004 in. glueline thickness.

TABLE XX

EFFECT OF NCO/OH RATIO ON LAP SHEAR STRENGTH OF PFPOI/UPFPOH POLYURETHANE ADHESIVE

NCO/OH	Lap Shear Strength, N/cm^2 (psi) -196°C	RT	94°C
1.3/1	2850 (4140)	1230 (1790)	172 (250)
1.5/1	3060 (4440)	1380 (2000)	152 (220)
1.6/1	2960 (4300)	1300 (1890)	179 (260)
1.7/1	2530 (3670)	1280 (1850)	179 (260)

Cure schedule variation yielded the following results (Table XXI).

TABLE XXI

EFFECT OF CURE SCHEDULE ON BOND STRENGTHS OF PFPOI/UPFPOH

Cure Schedule	Avg Lap Shear Strength, N/cm^2 (psi) -196°C	RT	94°C
5 days at 180°F	2140 (3100)	990 (1440)	269 (390)
3 days at 200°F	1950 (2830)	690 (1000)	110 (160)
5 days at 200°F	2070 (3000)	710 (1030)	145 (210)
2 days at 225°F	1470 (2130)	310 (450)	76 (110)
3 days at 225°F	1780 (2580)	483 (700)	90 (130)
2 days at 250°F	920 (1330)	290 (420)	90 (130)
3 days at 250°F	1630 (2370)	317 (460)	117 (170)

It can readily be seen that the shorter/hotter cures promote a deleterious effect on bond strengths. All the failed specimens showed almost complete adhesive failures.

H. Liquid Oxygen Impact Sensitivity of a Simulated Aluminum/Aluminum Bond

A series (41) of specimens which were designed to simulate a bond configuration with exposed adhesive fillets was submitted for LOX compatibility testing. The specimens were prepared as follows:

1) 11/16 in. diameter discs of 0.020 in. 2024-T6 clad aluminum were punched, rinsed in trichlor, and etched with standard FPL dichromate/sulfuric acid solution.

2) After rinsing with distilled water and drying, a small amount of mixed/de-aired PFPOI/UPFPOH (Batch 8) adhesive was applied to the center of each disc.

3) 0.004 in. Shim wires were laid in and a second 1/2 in. diameter disc, prepared as above, was centered over the larger disc and gently pressed in place.

4) The resulting specimens were cured 5 days at 82°C.

This configuration, which allowed exposure of a fillet of cured adhesive ~3/32 in. wide around the periphery of the assembled discs was then tested under liquid oxygen and 10 kg-m impact.

Results were inconclusive. Two of the set of twenty tests resulted in a visible flash (in the darkened test fixture) with no audible report.

Examination of the tested specimens which reportedly produced a flash showed no difference from the other specimens. If serious degradation had occurred in the adhesive, then evidence of scorching (at least a discoloration) would probably be expected. The possibility of a reaction involving the metal itself (discs or shim wire) cannot be ruled out.

I. Torsional Braid Analysis Studies

Four strand braids of 181-E glass yarn were impregnated with the PFPOI/UPFPOH polyurethane adhesive to check the low temperature characteristics of the system. Three braids were prepared using NCO/OH ratios of 1.4/1, 1.6/1 and 1.8/1. The results of the torsional braid analysis (TBA) are presented in Figures 4, 5 and 6.

The "relative rigidity" plotted on the abscissa is developed by the ratio of squares of the frequency of the torsional pendulum at a given temperature and that of the "stiffest" (in this case at -180°C). The glass transition can be seen to occur at ~20°C in all cases.

The most significant differences can be discerned between the three specimens in the cryogenic region. A transition is occurring at <-180°C at 1.4/1 NCO/OH, at ~-170°C at 1.6/1 and ~-160°C at 1.8/1. This transition may be expected to influence cryogenic performance and will probably be best evaluated in adhesive applications by peel specimens.

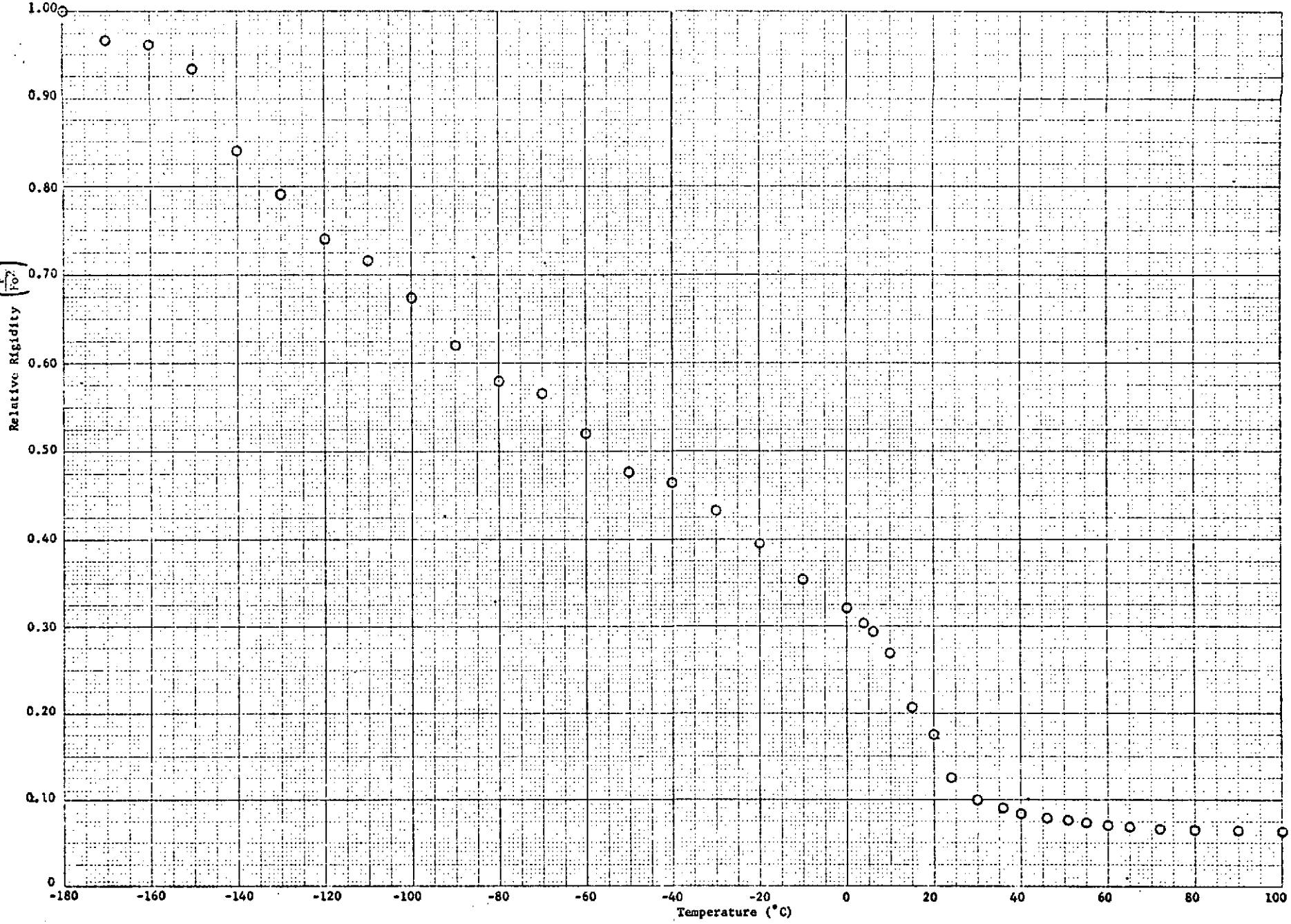


Figure 4. TBA Curve of PFPOI/UPFPOH Polyurethane at NCO/OH of 1.4/1

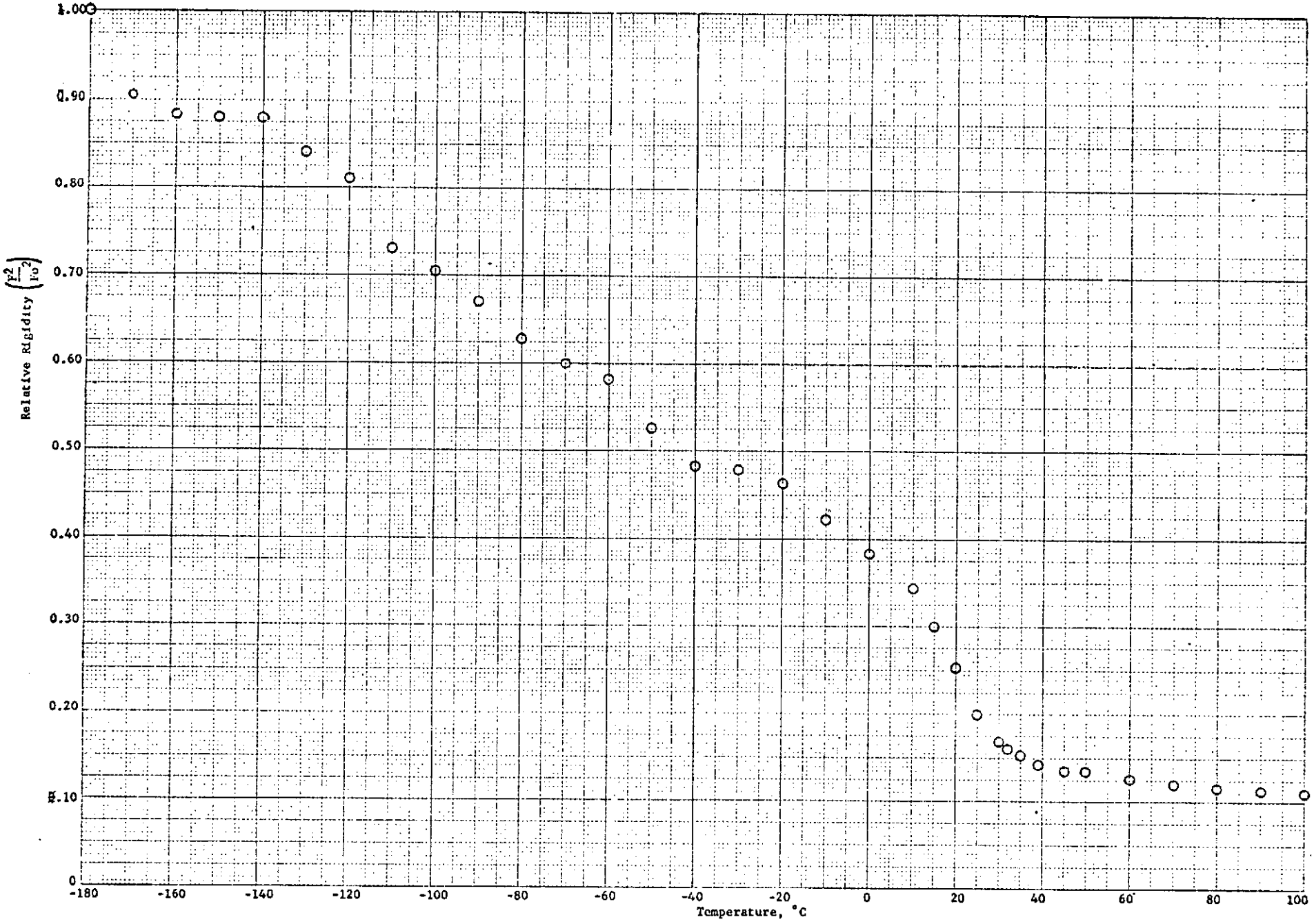


Figure 5. TBA Curve of PFPOI/UPFPOH Polyurethane at NCO/OH of 1.6/1

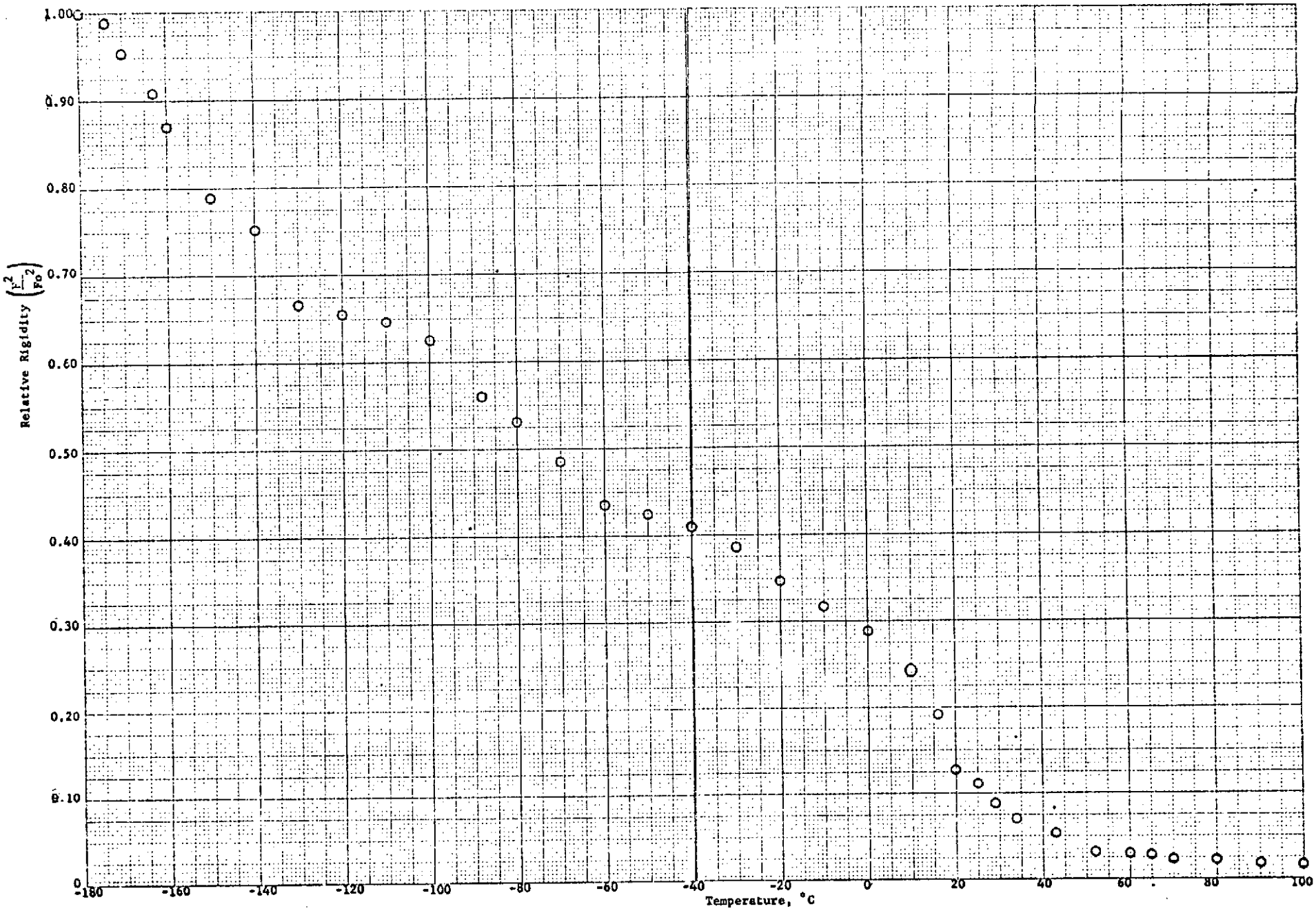


Figure 6. TBA Curve of PFPOI/UPFPOH Polyurethane at NCO/OH of 1.8/1

II - PRIMER STUDY

Previous reports have described primer studies in conjunction with the PFPOI/UPFPOH polyurethane system. These efforts utilized commercial primers which had resulted in marked improvement in all bond parameters when used in conjunction with commercial polyurethane adhesives. In no instance was there a significant improvement in bond strengths of the PFPOI/UPFPOH highly fluorinated polyurethane. These discouraging results have been initially attributed to poor wetting of the primed metal substrate and to the very low number of polar bonding sites in the fluoro-urethane.

We have previously evaluated the following primer systems:

DC-6020
DC-6020 (hydrolyzed)
DC-6040
A-1100

Similar lack of response was found when Dow Corning's 1200 primer was utilized. This primer, which is successfully utilized with polyurethane adhesives as well as the fluoro-silicone polymers, was expected to provide a more amenable bonding surace than those previously evaluated. The results are shown below:

	Tensile Lap Shear Strength, N/cm^2 (psi)		
Batch No.	-196°C	RT	94°C
8 (329-14) Unprimed	2700 (3910)	990 (1440)	193 (280)
8 (329-14) Primed	2320 (3370)	1020 (1480)	190 (275)

Consultation with Dr. Edwin Plueddleman of Dow Corning Corporation resulted in suggestion of two new primer systems for use in conjunction with the PFPOI/UPFPOH polyurethane. Preliminary results were encouraging.

Both primers are solutions (5-10%) of silane modified epoxies. Adherend preparation involved standard FPL etch, followed by spray application of the primer and a 2 hour air dry. The PFPOI/UPFPOH adhesive was then applied, 0.004 in. shim wire placed in the bondline, and the adhesive cured 5 days at 82°C (Table XXII).

TABLE XXII

EFFECT OF PRIMERS

Primer	Lap Shear Strength, N/cm^2 (psi) (Avg)			T-Peel, N/cm (lb/in.) (Avg)	
	-196°C	RT	94°C	-196°C	RT
None (Control)	3140 (4560)	1150 (1670)	262 (380)	5.25 (3.0)	9.62 (5.5)
DC 1205	3650 (5290)	1780 (2580)	331 (480)	11.20 (6.4)	24.2 (13.8)
XZ-8-5066	1080 (1560)	1400 (2030)	275 (400)	4.72 (2.7)	3.67 (2.1)

Almost total adhesive failure was found in the unprimed control while cohesive failure was achieved in primed substrates.

Repeat of this work gave the following excellent results (using Batch 9 of the PFPOI/UPFPOH system) (Table XXIII).

TABLE XXIII

EFFECT OF PRIMERS
(Repeat)

Primer	Lap Shear Strength, N/cm^2 (psi) (Avg)			Bell Peel, N/cm (lb/in.) (Avg)	
	-196°C	RT	94°C	-196°C	RT
None (Control)	3620 (5250)*	1320 (1910)*	228 (330)*	5.3 (3.0)*	6.7 (3.8)*
DC 1205	4310 (6250)	2210 (3200)	324 (470)	24.1 (13.8)	14.5 (8.3)
XZ-8-5066	1050 (1530)	1300 (1890)	282 (410)	5.3 (3.0)	12.1 (6.9)

* Adhesive failure.

III - WELD-BOND STUDIES

A. Literature Survey Covering Weld-Bond Technology

A preliminary search covering weld-bond technology was completed. In depth studies are essentially non-existent. The most appropriate reports uncovered thus far are those published by Lockheed-Georgia Company under Air Force Materials Laboratory sponsorship (previous Contract Report Number AFML-TR-70-22, and currently under Contract No. F33615-71-C-1716). These reports generally cover fabrication, metal surface preparation, and testing of a series of commercially available adhesives in a weld-bond configuration.

No particular information is disclosed on the bulk properties of the various adhesives other than that as obtained in adhesive applications. The normal adhesive evaluation techniques are utilized with appropriate modification to accommodate the geometry required for spot-welding. These techniques include lap shear, creep, peel, and wedge testing under various static/dynamic load conditions in typical weathering and humidity environments.

Consultation with recognized specialists in weld-bond technology were arranged. These conversations allowed a more realistic appraisal of the actual prerequisites in weld-bond adhesive properties.

B. Spot-weld Bonding

Preliminary investigations of spot-weld adhesive bonding (weld-bonding) applications were begun. Teledyne-Ryan Corporation prepared a few samples using the PFPOI/UPFPOH system in conjunction with various metal (clad 2024-T6) surface preparations to evaluate the weldability of the uncured material. The specimens were left with the Project Officer at MSFC for evaluation. The procedures followed are outlined as follows:

Etch Procedure	Time After Mixing of Adhesive (hr)	Weld Appearance (Cross-section)
Standard dichromate etch	1	Slight metal splash*
	4	" " "
Dichromate etch and wire brush	1	Very good
	4	" "
Spotweld etch	1	Excellent
	4	"
Spotweld etch and wire brush	1	Excellent
	4	"

* The weld-spot is not perfectly circular. Cross-section shows ~40% nugget volume which is not necessarily centered on the faying surfaces.

It is desirable that the surface resistivity of the metal samples be less than ~100 μohms for a quality weld. The standard dichromate etch results in a resistivity of >200 μohms which does not yield as high quality welds as are obtained by using other procedures.

The spotweld etch is described as a hydrofluosilicic acid treatment containing a Nacconol wetting agent which apparently leaves a protective film over the cleaned metal surface, thus allowing a reasonably long hold time between etching and subsequent spotweld operations. Resitivities of 60-70 μohms are routinely obtained using this procedure. The effect of this etch on the adhesive characteristics of the PFPOI/UPFPOH system is unknown at present.

Wire brushing is another method of surface preparation which results in a very low surface resistance which has a relatively short hold time.

These tests are only preliminary and were intended to show: 1) weldability of the uncured adhesive, and 2) pot-life of the adhesive is not a deterrent to large area bonding operations. In fact, the only significant disadvantage apparent from these brief experiments may be one of viscosity control at elevated temperatures. A significant amount of adhesive had flowed out of the faying volume during cure (225°F for 60 hours). If this is indeed a problem it is probably most readily surmounted by utilization of a conductive filler such as aluminum powder.

C. Weld-Bond Studies

These preliminary tests,coupled with an acceptable level of liquid oxygen compatibility, allowed further testing to proceed in the weld bond configuration. Toward this end, we prepared two weld-bonded panels with a total of 58 spotwelds. The panels were prepared in the following fashion:

1. 0.040 x 4.0 x 30.0 in. sheets of 6061-T62 aluminum alloy were vapor degreased (trichloroethylene).

2. Deoxidized with Raco-032 (an aqueous chromic/nitric acid system).

3. Rinsed with de-ionized water and dried at 66°C. Surface resistivity was 40 μohms.

4. The mixed and de-aired PFPOI/UPFPOH fluorinated polyurethane was applied to one faying surface and a series of spotwelds accomplished on approximately one inch centers midway in the one inch overlap surfaces.

A metallographic examination of the weld before curing of the adhesive (on a five weld specimen) showed very good welds well within specifications. The 3/8 in. dia. electrode results in a nominal 0.163 in. diameter nugget with penetration well within the 43<%>63 top and 58<%>73 bottom requirements. Single spot tensile shear tests (240 and 230 Newtons) easily exceed the 206 Newton minimum.

We simultaneously prepared a smaller panel of 15 spots for joint strength measurements and fatigue studies.

The Raco-032 (aqueous chromic/nitric acid) deoxidizer is not generally suitable for high quality adhesive bonds and it appears that this same situation applies here. Adhesive failure was encountered in every case. The quality of the welds is reflected by both the strengths and examination of the failed specimens. No indication of any scorching or degradation of the adhesive is visible. Tensile shear results are shown below in Table XXIV.

TABLE XXIV

WELD-BONDED LAP SHEAR RESULTS
USING 6061-T62 ALUMINUM ADHERENDS
DEOXIDIZED WITH RACO 032
($\sim$0.4 in^2 Bonded Area)

Temperature, °C	Failing Load, N (lb)
RT	236 (530)
-196	309 (695)
RT	565 (1270)
94	240 (540)
-196	476 (1070)

* Spotweld only, no adhesive.

D. Capillary Filled Adhesive Bonded Spotwelds

The capillary "fill-in" technique of the previously spot-welded panels was accomplished. The efficiency of this method was expected to be strongly influenced by viscosity parameters since the faying surfaces are in intimate contact after the spotwelding process. To obtain as low a viscosity as we could (for this preliminary investigation) a deviation from standard PFPOI/UPFPOH techniques was employed.

Simple admixture of the basic hydroxyl-terminated polyperfluoro-propylene oxide (PFPOH) with 4-chloro-trifluoro-m-phenylene diisocyanate at room temperature results in a heterogeneous mixture. Heating the stirred mixture at 100°C for $\sim$1 hour results in a clear homogeneous mixture at room temperature which is quite fluid. We followed this technique (using stoichiometry such that the overall NCO/OH ratio was varied at 1.4/1, 1.6/1 and 1.8/1) in the capillary adhesive experiment (Table XXV).

After the initial heating period, a bead of the fluid prepolymer mixture was applied to the upper edge of the previously spotwelded faying surfaces (layed horizontally) and placed in an oven at 82°C. After $\sim$120 minutes, a bead began to appear at the other (lower) edge. The adhesive was cured at 82°C for three days.

When the panels were sawed into individual specimens, and tested, it was obvious that the material in the interfacial area was soft and certainly not completely cured, while that material which remained (in the initial bead) was strong and adequately hardened. In addition, the freshly failed specimens had an odor of the diisocyanate. This lack of cure was not expected

TABLE XXV

CAPILLARY FILLED ADHESIVE/SPOTWELD JOINTS
(~0.5 in^2 Bonded Area)

NCO/OH Ratio	Failing Load (Avg), N (lb) RT	94°C	-196°C
1.4/1	378 (850)	242 (545)	367 (825)
1.6/1	316 (710)	234 (525)	347 (780)
1.8/1	327 (735)	231 (520)	320 (720)
1.4/1*	636 (1430)	236 (530)	--
1.6/1*	614 (1380)	231 (520)	--
1.8/1*	445 (1000)	238 (535)	--

* Additional 48 hours at 107°C.

The remaining sales were cured an additional 48 hours at 107°C. The values were greatly upgraded to closely approximate those obtained from the regular weld-bonding process. No odor of residual isocyanate was apparent nor was there any evidence of lack of cure. Preliminary results (using the same technique of precooking monomers) have been obtained on standard FPL etched lap shear couples (Table XXVI).

TABLE XXVI

LAP SHEAR STRENGTH OF COUPONS

NCO/OH Ratio	Lap Shear Strength (Avg), N/cm^2 (psi) -196°C	RT	94°C
1.3/1	2800 (4060)	1230 (1790)	174 (252)
1.5/1	3060 (4440)	1380 (2000)	152 (220)
1.6/1	2960 (4300)	1300 (1880)	179 (260)
1.7/1	2300 (3340)	1280 (1850)	172 (250)

Adhesive failure was again the rule. No evidence of lack of cure was noticeable.

We successfully re-evaluated the capillary flow method of adhesive application to previously spot-welded aluminum adherends. Earlier experiments utilized a very low viscosity system prepared by simply heating a mixture of 4-chloro-trifluoro-m-phenylene diisocyanate at 100°C until a

homogeneous mixture was obtained at room temperature (~1 hour). This mixture was expected to reault in improved wetting and would be expected to yield superior results over the standard PFPOI/UPFPOH prepolymer mixture.

We decided to repeat the test using the standard PFPOI/UPFPOH system in conjunction with primed (DC-1205) adherends.

Metal surface (0.040 in. 6061-T62 aluminum) preparation was as previously described, and included alkaline cleaning, followed by Raco-032 deoxidizing solution and de-ionized water rinse. The DC-1205 primer was sprayed on and allowed to air dry for 2-1/2 hours. (Out-time studies on the weldability of the thus-primed adherends indicates that at least 72 hours may elapse and still achieve high quality welds well above 220 Newtons compared to 206 Newton specification minimum.

Spot-welding was accomplished on approximately one inch centers with a one inch overlap of the faying surfaces.

The PFPOI/UPFPOH components were mixed in overall NCO/OH ratios of 1.4/1, 1.6/1 and 1.8/1.

The degassed adhesive was applied as a bead along the exposed edge of the upper faying surface. The coupons were placed (horizontally) in a forced air oven and cured at 82°C for 5 days.

The samples were then cut into ~0.8 in. wide specimens centered around the individual spot-welds. Results are presented in Table XXVII below.

TABLE XXVII

SHEAR STRENGTH OF PFPOI/UPFPOH BONDED SPOTWELD JOINTS BY THE CAPILLARY TECHNIQUE (DC-1205 PRIMED)

NCO/OH Ratio	Failing Load (Average) (~0.8 in^2 Overlap), N, (lb) -196°C	RT
1.4/1	*	747 (1680)
1.6/1	*	751 (1690)**
1.8/1	*	631 (1420)

* Premature metal failure at ~800 Newton load.
** Premature metal failure at ~750 Newton load.

In all cases a cohesive failure was observed with complete coverage of the faying surface invariably found. No indication of incomplete cure was found. The failed (room temperature) samples all have taken a permanent set in the bonded area.

E. Weld-Bond Studies Using Primed Aluminum Adherends

We previously reported the ready weldability of the PFPOI/UPFPOH system and, in the previous section, similar success with dried DC-1205 primer. When we tried to spot-weld through PFPOI/UPFPOH applied to primed aluminum adherends, however, we found a no weld condition. Evidently the combined high resistivities disallows passage of adequate currents for even the beginning of fusion and subsequent welding.

To reduce the effective resistance we decided to add aluminum powder (MD-105) to the PFPOI/UPFPOH system. We began by adding an equal amount of dried MD-105 to the mixed adhesive (50% loading). This loading level, while offering the lowest resistivity, suffers from a very high viscosity limitation. Bond strengths indicate only slight improvement in properties with application of the DC-1205 system previously shown to be effective in the unprimed system. The results are listed in Table XXVIII below.

TABLE XXVIII

BONDED STRENGTH OF MD-105 FILLED (50%)
PFPOI/UPFPOH (NCO/OH = 1.8/1)

	Lap Shear, N/cm^2 (psi)			Bell Peel (avg) N/cm (lb/in.)	
	-196°C	RT	94°C	-196°C	RT
Primed (DC-1205)	2500 (3630)	1380 (2000)	317 (460)	17.5 (10.0)	23.5 (13.5)
Unprimed	2310 (3350)	1250 (1820)	338 (490)	16.6 (9.5)	17.2 (9.8)

Cohesive failure was found in the room temperature and 94°C tests while adhesive failure (probably in the primer) was found in the -196°C specimens.

When we attempted to weld through the mixed adhesive, the very high viscosity brought about "blowing" of the forming weld. Therefore, we decided to go to lower filler loadings with good results.

Adhesive values are shown below in Table XXIX. These results were obtained on 2024-T6 aluminum which had been FPL etched and subsequently primed with DC 1205.

TABLE XXIX

EFFECT OF MD-105 LOADING LEVEL ON BOND STRENGTH OF DC-1205 PRIMED 2024-T6 ALUMINUM (0.063 in.) (NCO/OH = 1.8/1)

Filler Loading, %	Lap Shear Strength (avg), N/cm^2 (psi)		
	-196°C	RT	94°C
9.1	*	1830 (2650)	200 (290)
16.6	3180 (4610)	1660 (2410)	234 (340)
23.1	3170 (4600)	1580 (2290)	234 (340)

* Metal failure at ~3300 N/cm^2 bond stress

The same failure modes encountered at 50% loading level were repeated.

Weld-bonding was then carried out using the primed metal previously described. In all cases an acceptable weld was obtained (230-245 Newtons). It was necessary to increase the voltage (from 1800V to 1900V) and hold for ~10 seconds under pressure before applying the voltage. Results are shown below in Table XXX.

TABLE XXX

STRENGTH OF WELD-BONDED PFPOI/UPFPOH/MD-105 JOINTS PRIMED WITH DC-1205

Filler Loading, %	Failing Load, N (lb) (~0.65 x 1 in. Overlap centered on spotweld) (0.40" Thick 6061-T62)		
	-196°C	RT	94°C
9.1	*	516 (1160)	276 (620)
16.6	*	520 (1170)	258 (580)
23.1	*	534 (1200)	262 (590)

* Metal failure at ~580 Newton load.

These acceptable results indicate that development of a spotweld/primer/adhesive system is a very strong probability.

F. Liquid Oxygen Compatibility Test Results

We submitted several samples of the PFPOI/UPFPOH system on aluminum substrates in various configurations (both primed and unprimed). These were transmitted to Marshall Space Flight Center for machining into sample sizes suitable for impact testing in liquid oxygen.

It was decided to have the samples finally shaped at MSFC because of the critical requirement of scrupulous cleanliness. The samples were submitted in the following (previously reported) configurations:

Sample No. 328-38A (weld bond samples, 2 panels, a total of 58 specimens)

1. 0.040 x 4.0 x 30.0 in. sheets of 6061-T62 aluminum alloy were vapor degreased (trichloroethylene).

2. Deoxidized with Raco-032 (an aqueous chromic/nitric acid system).

3. Rinsed with de-ionized water and dried at 66°C. Surface resistivity was 40 μohms.

4. The mixed and de-aired PFPOI/UPFPOH fluorinated polyurethane was applied to one faying surface and a series of spotwelds accomplished on approximately one inch centers midway in the one inch overlap surfaces.

5. Cure of 5 days at 82°C was then carried out.

Sample No. 329-50B (primer evaluation)

1. A 4 x 8 x 0.020 in. 2024-T6 clad aluminum panel was etched (FPL) and coated with DC-1205 primer and dried at room temperature.

Sample No. 329-50C

1. Another panel, primed as above, was coated with an overlay coating (0.005 in.) of the PFPOI/UPFPOH adhesive.

Sample No. 329-50D

1. Two panels were primed and air dried, then bonded together (.004 in. glueline thickness) with the fluorinated polyurethane to form a bonded sandwich.

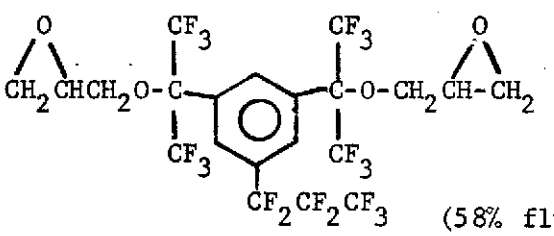
The last three specimens were then cured five days at 82°C.

During the machining operation at MSFC, sévere contamination by normal shop techniques occurred, resulting in rejection of the primed systems (329-50B, C and D). The wald bonded specimens (329-38A) were saved by carefully sanding all the exposed surfaces and thoroughly washing and rinsing with trichloroethylene.

Results of impact testing at 10 kg-m loading in liquid oxygen at 69 N/cm^2 was quite satisfactory. Two sets of twenty specimens each show no failures. The tested specimens reportedly were severely deformed (i.e., metal deformation).

G. Alternate Primer Systems

Dr. J. R. Griffith (Naval Research Laboratories, Washington D.C.) and co-workers have developed a series of partially fluorinated epoxy resins which have the potential of serving as alternate primer systems to the efficient DC 1205 presently used. These materials, which should be inherently less sensitive to liquid oxygen, are not commercially available and current funding disallows their synthesis. Dr. Griffith has graciously offered us a small sample of the following material (a liquid resin at room temperature), which should be received in the near future.



(58% fluorine)

Substitution of this material into DC 1205 primer on a one to one molar basis for the incumbent DER 331 should not prove too difficult (providing solubility problems do not occur).

We had not received the sample at the time of writing of this report.

H. Large Batch Preparation of PFPOI/UPFPOH

During the final phases of the contract a large batch of the PFPOI/UPFPOH polyurethane was prepared and the two components shipped to the Contracting Officer (MSFC). The total shipment consisted of 1044.6 g of PFPOI and 124.5 g of UPFPOH. The molecular weight of the PFPOH precursor was 1430.

PHASE II
CONCLUSIONS

Improvements and refinements in preparative techniques have resulted in marginal liquid oxygen compatibility for the PFPOI/UPFPOH fluorinated polyurethane system. The expenditure of these efforts which were not anticipated in the beginning of Phase II, resulted in necessary diminution of effort on the second major objective.

However, significant progress was made on the weld-bond portion of this phase. Both types of weld-bond operations (weld-through of the uncured adhesive and capillary fill-in of previously spot-welded adherends) have been shown to be readily accomplished. High quality welds are routinely attainable through the uncured adhesive. Corresponding adhesive values have shown some deficiency.

Utilization of a commercially available primer system (DC-1205) has been shown to be quite efficient in upgrading the adhesive characteristics of the PFPOI/UPFPOH system. This same primer is also usable as a weld-through system suitable for capillary fill-in techniques. However, the same combination of primer/adhesive (i.e., PFPOI/UPFPOH and DC-1205) is not suitable for weld-through applications. These difficulties have been shown to be readily surmounted by incorporation of MD-105 aluminum powder as a conductive filler for the adhesive. Samples which were intended to establish LOX compatibility of the primer/adhesive system were inadvertently contaminated during preparative machining operations at Marshall Space Flight Center.

Compatibility of the duplex (adhesive/primer) system must be established before reliable spot-weld/adhesive characteristics can be defined. Alternate, inherently more LOX compatible primer systems may be readily attainable through incorporation of the fluorinated epoxy systems mentioned at the close of the text.

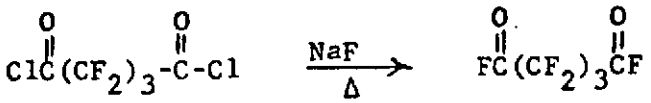
Supplemental effort on metal surface preparation, to encompass commercially available alternate spot-weld etchants should be extended.

Weld-bond and adhesive parameters alone should be evaluated in both primed and unprimed configurations, to ultimately result in an optimized liquid (gaseous) oxygen compatible metal joining process.

EXPERIMENTAL

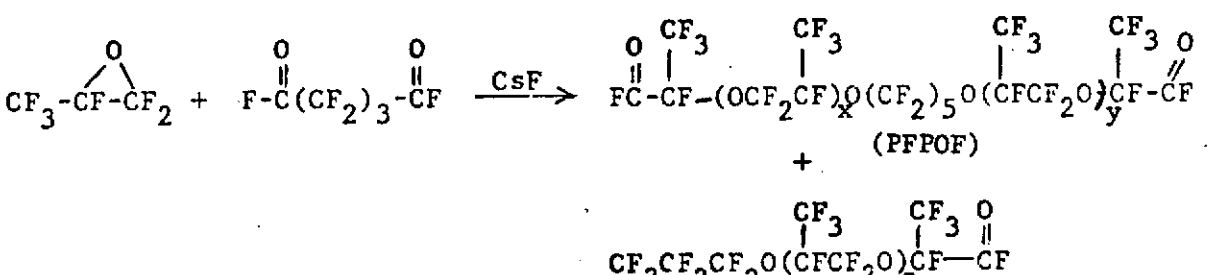
TYPICAL PREPARATION OF HYDROXYL-TERMINATED POLYPERFLUOROPROPYLENE OXIDE [PFPOH]

A. Preparation of Perfluoroglutaryl Fluoride



Sodium fluoride (552 g, 13.2 mole) was dried 72 hours at 316°C in a five-liter flask. The flask was removed from the oven and allowed to cool under a dry nitrogen flow. Redistilled sulfolane (1580 ml) was added and stirring begun. Perfluoroglutaryl chloride (1000 g, 3.69 mole) was added over a period of three hours. The temperature was kept below 35° during the addition. Heat was applied and the reaction mixture allowed to reflux (48°C) for 3 hours. After standing (under nitrogen) overnight, the volatile material (<49°C b.p., 627 g) was isolated by distillation and then re-distilled through a helices-packed, 96-cm vacuum-jacketed column. The fraction boiling at 45°-46°C was collected. Purity (by VPC) was >99%, and the yield was 513 g.

B. Polymerization of Perfluoropropylene Oxide



Cesium fluoride (89.2 g, 0.68 mole) was dried in a two-liter reaction flask at 315°C for 5 days. The dried material was allowed to cool under dry nitrogen. The partially solidified mass was broken up into small lumps and doubly distilled diglyme (b.p. 162°-163°C, 330 ml) was added. The mixture was then stirred for 30 minutes. Perfluoroglutaryl fluoride (231 g, 0.95 mole) was added over a 90 minute period, with the temperature of the stirred reaction mixture maintained at 10°-11°C with a dry ice/acetone bath. The finely dispersed slurry was stirred an additional 30 minutes at 10°-11°C. The mixture was cooled to -13°C and perfluoropropylene oxide (50 g, 0.30 mole) was added over a 40-minute period at this temperature. The reaction mass was allowed to warm to 10°C and the remainder of the epoxide (1950 g, 11.70 mole) was added (T = 9°-10°C) over a four-hour period. Stirring was continued overnight at ambient temperatures. Filtration

through fine fritted glass funnels produced 1868 g of a clear, colorless mobile liquid. Fractional distillation under reduced pressure yielded the following cuts:

	Boiling Range, °C	mm Hg	Total Weight	
Cut I	27-40	0.7-0.8	297.8 g	
Cut II	42-49	0.09-0.10	485.0 g	
Cut III	49-63	0.10-	14.0 g	
Cut IV	68-78	0.2-0.3	19.0 g	
			815.8 g	collected and set aside

51.0 g of material was collected in the pre-pump dry ice/acetone traps.

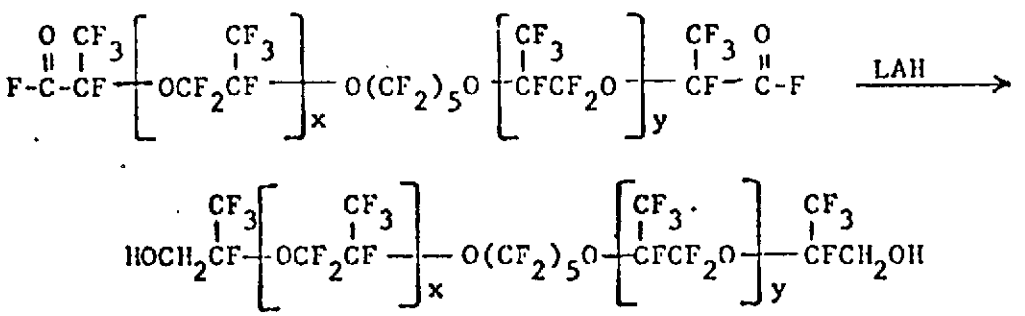
The molecular weight of the residue was determined by VPO measurements in Freon 113 using benzil as a standard. A plot of the data resulted in an essentially straight line with an extrapolated zero-zero intersection. Acid fluoride number was determined by the following procedure:

Place 75.00 ml of standardized 0.1N NaOH in a 250 ml flask. Add 10 ml of 5% pyridine in water solution. Weigh in 3 to 4 milliequivalents of PFPO acid fluoride. Stopper the flask and shake for at least 2 hours and until clear. Titrate with standardized 0.1N hydrochloric acid to the phenol-phthalein end point.

$$EW = \frac{(2000)\ (\text{Sample Weight})\ (\text{grams})}{(\text{ml Base} \times \text{N Base}) - (\text{ml acid} \times \text{N acid})}$$

Results:	Equivalent Weight (as above)	Molecular Weight by VPO in Freon 113	Indicated Functionality
	620,624	1246,1237	2.00

C. Reduction of Acyl Fluoride-Terminated Polyperfluoropropylene Oxide



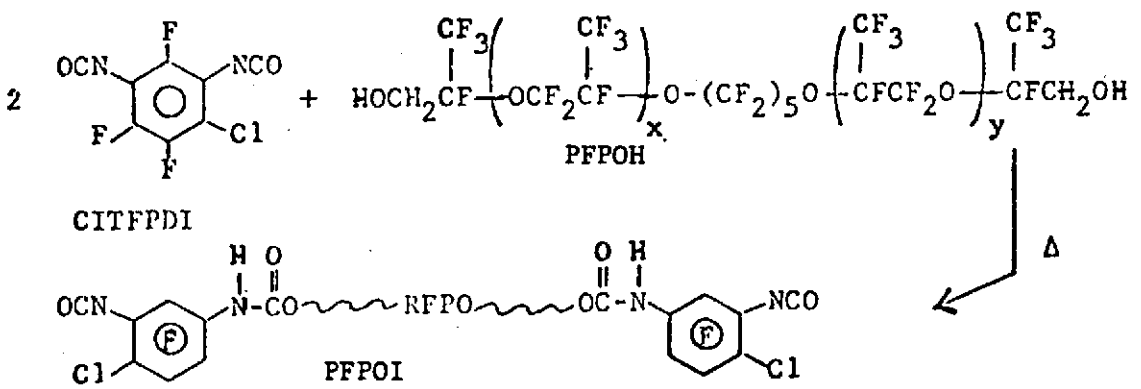
PFPOH

Lithium aluminum hydride (72 g, 2.68 mole) was carefully added to dry tetrahydrofuran (3000 ml) in a 12 liter Morton flask and stirred for one hour. Crude, residual polyperfluoropropylene oxide (1027 g) was added over a four-hour period using external cooling to maintain the temperature between 10°-20°C. The gray slurry was vigorously stirred throughout the addition and then for an additional three hours. Wet (20%, 500 ml) THF was cautiously added over a two-hour period and stirred for an additional 30 minutes. The gray emulsion was then cautiously poured into 5 liters of 5% sulfuric acid with stirring and allowed to stand overnight. The clear fluorocarbon layer was isolated, dissolved in ether (2 liters) and dried 24 hours ($MgSO_4$). The ether was then removed from the filtered solution, yield 938 g of crude product. Vacuum fractionation resulted in the following fractions:

Fraction	Boiling Range	mm Hg	Total Weight
1	26-104	0.4-0.5	45.0 g
2	130-168	1.0-0.5	867.0 g
			912.0 g collected

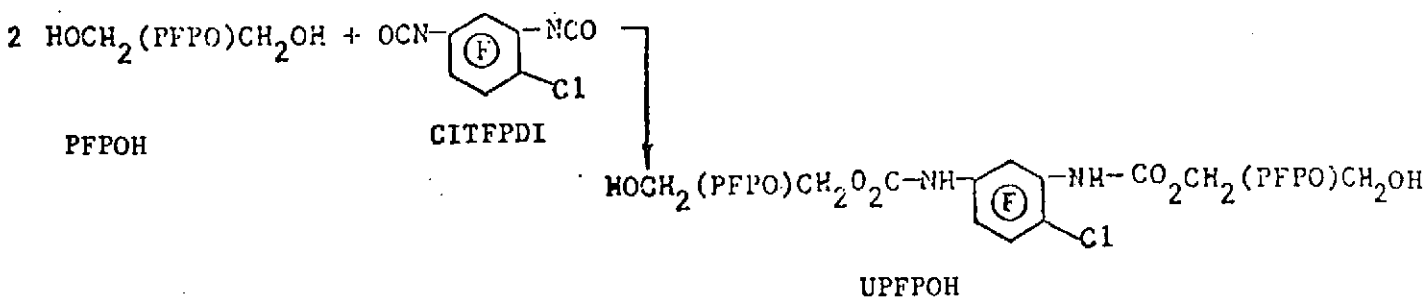
In addition, 16 g of low boiling material was caught in the dry ice/acetone traps.

D. Preparation of Isocyanate-Terminated Polyperfluoropropylene Oxide Prepolymer (PFPOI)



Hydroxyl-terminated polyperfluoropropylene oxide PFPOH (125.0 g, 0.100 mole) was charged to a resin kettle under dry nitrogen and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate (50.0 g, 0.202 mole) was added. The two-phase mixture was stirred as the temperature was slowly raised (oil bath). The solution became homogeneous when the temperature reached 93°C. The progress of the reaction was followed by noting the disappearance of the infrared band at 3400 cm^{-1} (-OH stretching) and the concurrent appearance and increase in the band at 3300 cm^{-1} (NH stretch). After stirring for 3-1/2 hours at a temperature of 90°-95°C, the system was thoroughly evacuated (at ~95°).

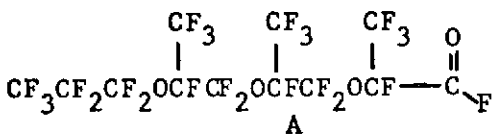
E. Preparation of Urethane-Extended Hydroxyl-Terminated Polyperfluoropropylene Oxide-UPFPOH



A mixture of PFPOH (25.0 g, 0.020 mole) and CITFPDI (2.63 g, 0.0105 mole) was stirred overnight at 90°-100°C under a dry N_2 atmosphere. Infrared spectroscopy indicated a complete disappearance of the N=C=O absorption at 2260 cm^{-1}.

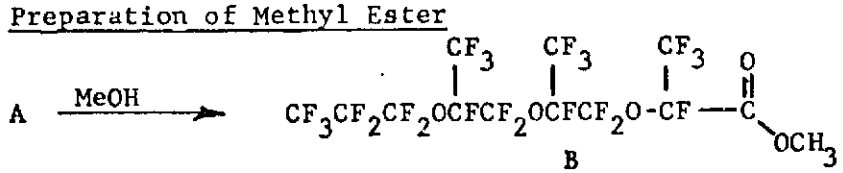
F. Isolation of Perfluoro-2,5,8-Trimethyl-3,6,9-Trioxa-dodecanoyl Fluoride A

The low molecular-weight components from the preparation of PFPOF were fractionally distilled under reduced pressure through a 1/4 in. helices-packed, vacuum-jacketed column (3/4 in. x 24 in.). The fraction boiling at 70°-74°C at 20-24 mm Hg was collected and analyzed. Vapor-pressure osmometry (using Freon TF solvent) yielded a molecular weight of 654. End group analysis yielded an acyl fluoride number of 660. These results indicate the title compound A (molecular weight 652).



A

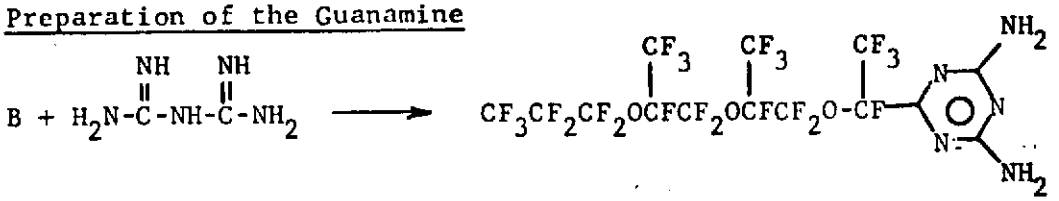
G. Preparation of Methyl Ester



B

The acyl fluoride A (33 g, 0.05 mole) was stirred with methanol (200 ml dried over 3A molecular sieves) overnight. Silica gel (~2 g) was added to destroy residual hydrogen fluoride, followed by filtration. The excess methanol was removed by decantation, and the crude product was fractionated under reduced pressure. The product (23.0 g) was flash distilled under vacuum pump pressure. Infrared spectrum indicates no residual acyl fluoride. VPC indicated >99% purity.

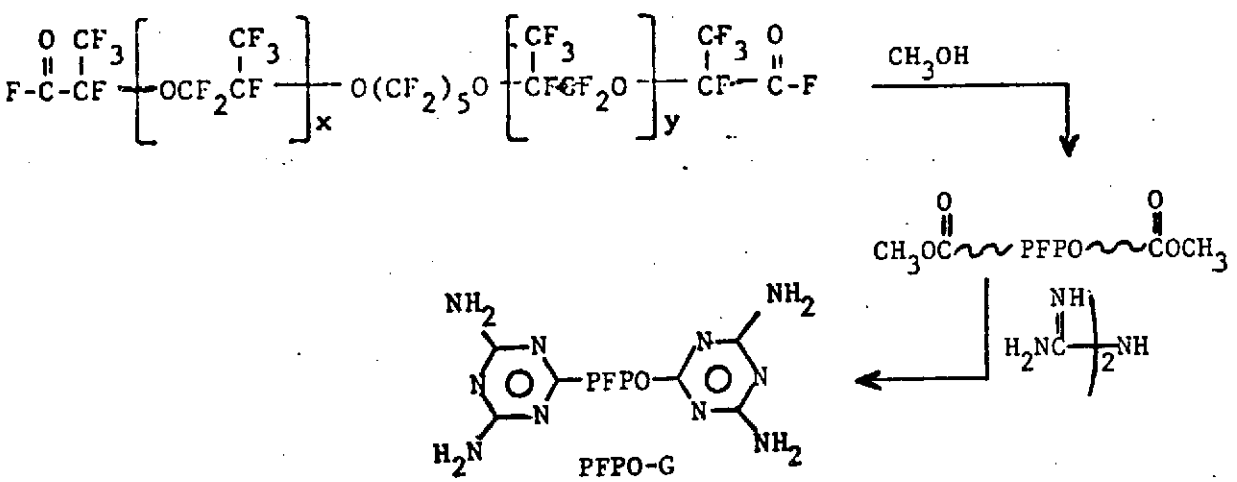
H. Preparation of the Guanamine



The methyl ester B (16.5 g, 0.025 mole) was mixed with dry methanol (20 ml) and a methanol slurry of biguanide (2.6 g, 0.026 mole) in 20 ml was added over a 15-minute period. A slight exotherm was noted (to 29°C) and the mixture cleared after 90 minutes. Stirring was continued overnight.

The clear solution was poured into 100 ml of water. The white waxy precipitate was filtered (with difficulty), washed thoroughly with water, and dried over the weekend. Yield: 15.2 g crude, m.p. 73°-75°C. The crude product was dried by azeotropic distillation with benzene (~0.25 g H_2O was noted). The bulk of the benzene was removed by decantation, with the last traces removed under reduced pressure at 95°C. The overall yield was 14.0 g (68%).

I. Preparation of the Bis-guanamine (PFPOG) Derived from PFPOF



The methyl ester was prepared from unfractionated difunctional PFPOF (mol. wt. 1381, acid equiv. 681) following the same procedure as described above. The distilled ester was collected at 144°-159°C/0.5 mm Hg.

The bis-guanamine was prepared as follows:

Biguanide (6.0 g) was suspended in dry methanol (400 ml) and 35.0 g of the methyl ester of PFPO was added with stirring over 1.5 hours. After overnight reflux, the solvent volume was reduced to ca. 100 ml under reduced pressure. The residual solution was then poured into water (1000 ml) with vigorous stirring. A stable suspension formed which would not

separate on standing. A saturated solution of sodium chloride (300 ml) was added with gentle stirring to break the emulsion. The precipitated polymer was isolated by filtration (with difficulty), and washed with water. The wet polymer was dried by azeotropic distillation using benzene. After cooling the residual benzene was removed by decantation. Acetone (160 ml) was then added to dissolve the precipitated polymer. The residual sodium chloride (2.6 g) was removed by filtration, and the filtrate dried over anhydrous magnesium sulfate. The solvent was removed under pump vacuum at 85°C, and 34.0 g of transparent solid PFPOG was recovered, mp 60°-72°C. Molecular weight (by VPO in acetone) was determined to be 1700. The infrared spectrum was consistent with the proposed structure, with no indication of residual ester or acid.

The following figures are reproductions of vapor phase-chromatographs obtained from the preparation of the 1268 molecular weight PFPOF mentioned in the text. Figure 7 shows the chromatograph of the crude unfractionated material as obtained following filtration to remove excess cesium fluoride catalyst. The double "envelope" shape described previously is clearly evident. Fractionation at reduced pressure has been facilitated by chromatography monitoring. The various component peaks have been previously identified (for higher molecular weight difunctional material) and samples of pure materials (probably isomeric mixtures) have been retained, allowing calibration of the instrument. Figures 8 and 9 are the chromatograms of fractionated difunctional PFPOH respectively. The various components are identified by molecular weight, obtained by the calibration technique described above.

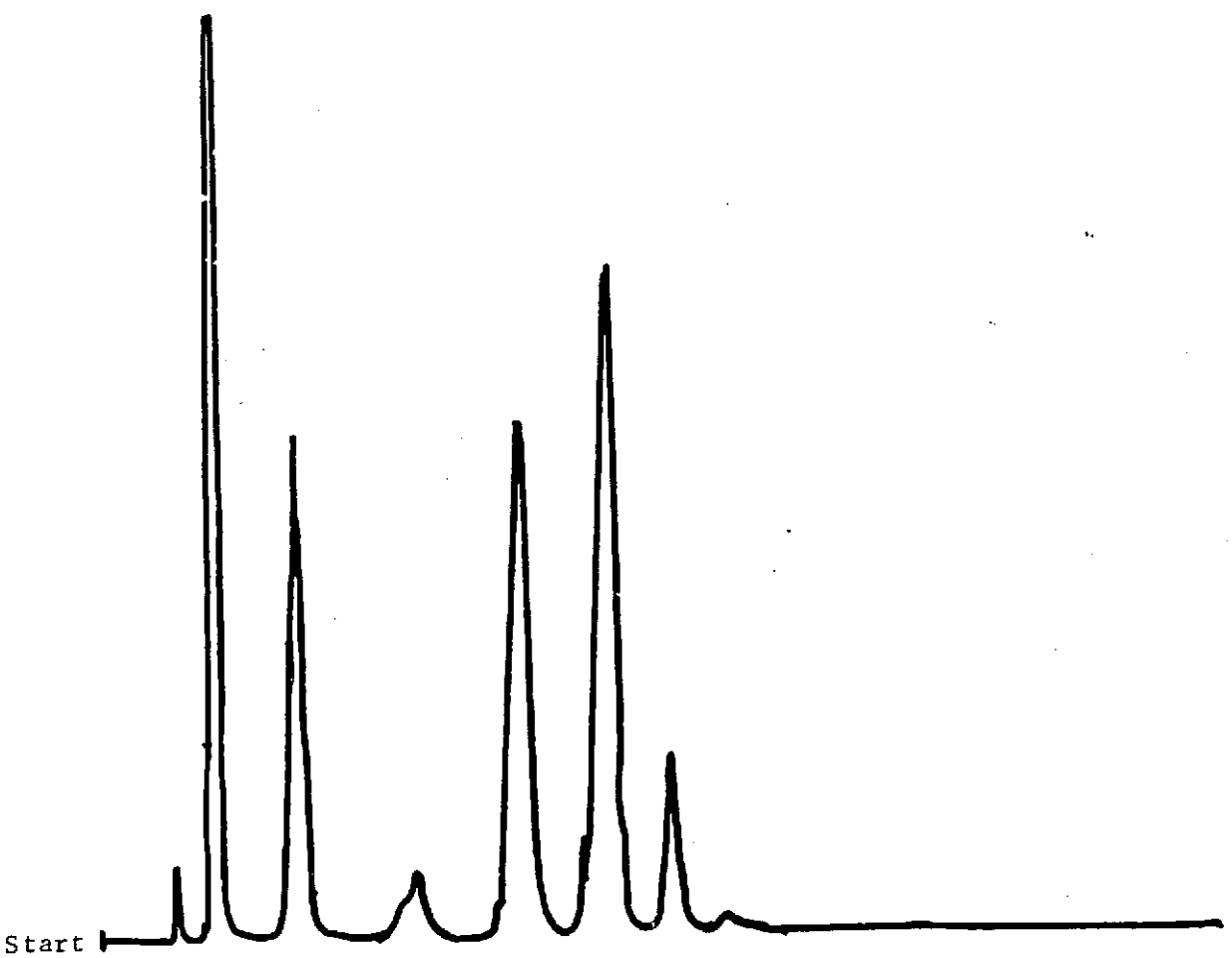


Figure 7. Gas Liquid Chromatograph of Crude Unfractionated PFPOF
Silicone rubber W-98 6' column
Column temp at start - 140°C
Program rate 10°C/min to 250°C

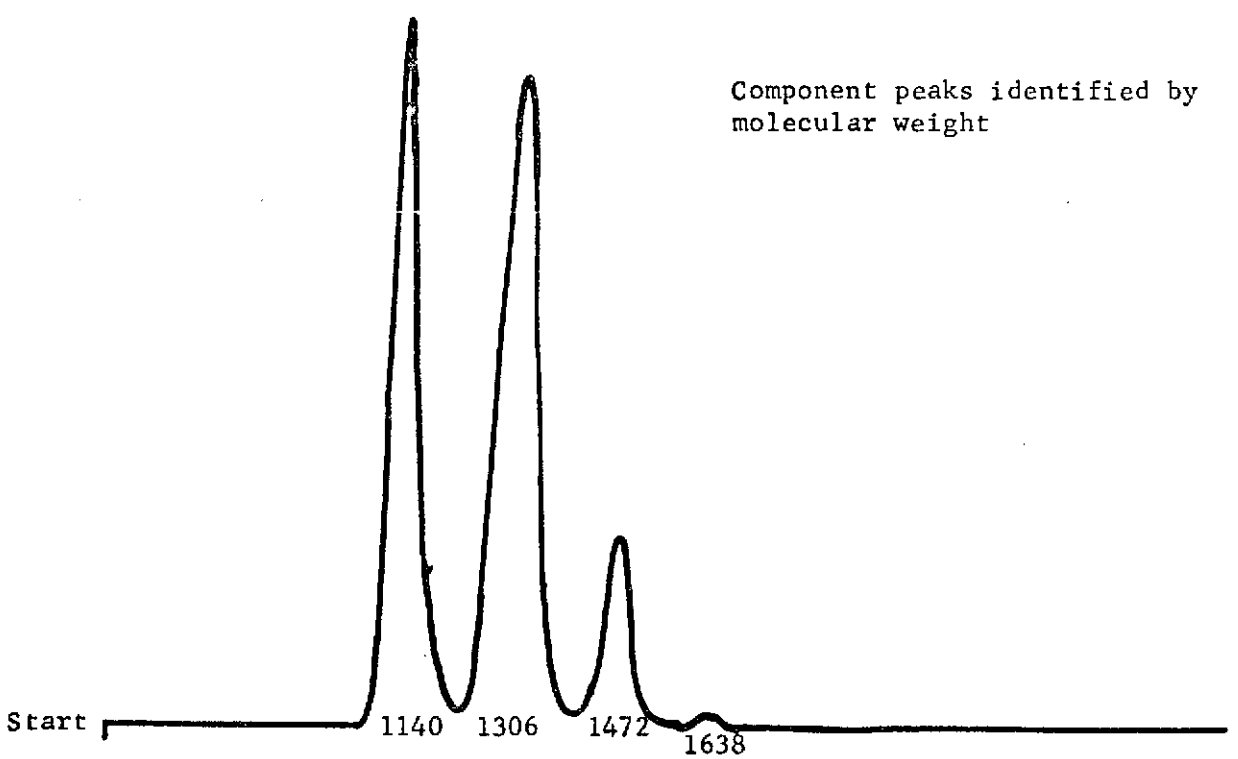


Figure 8. Gas Liquid Chromatogram of Difunctional PFPOF
Silicone rubber W-98 6' column
Column temp at start -140°C
Program rate 10°C/min to 250°C

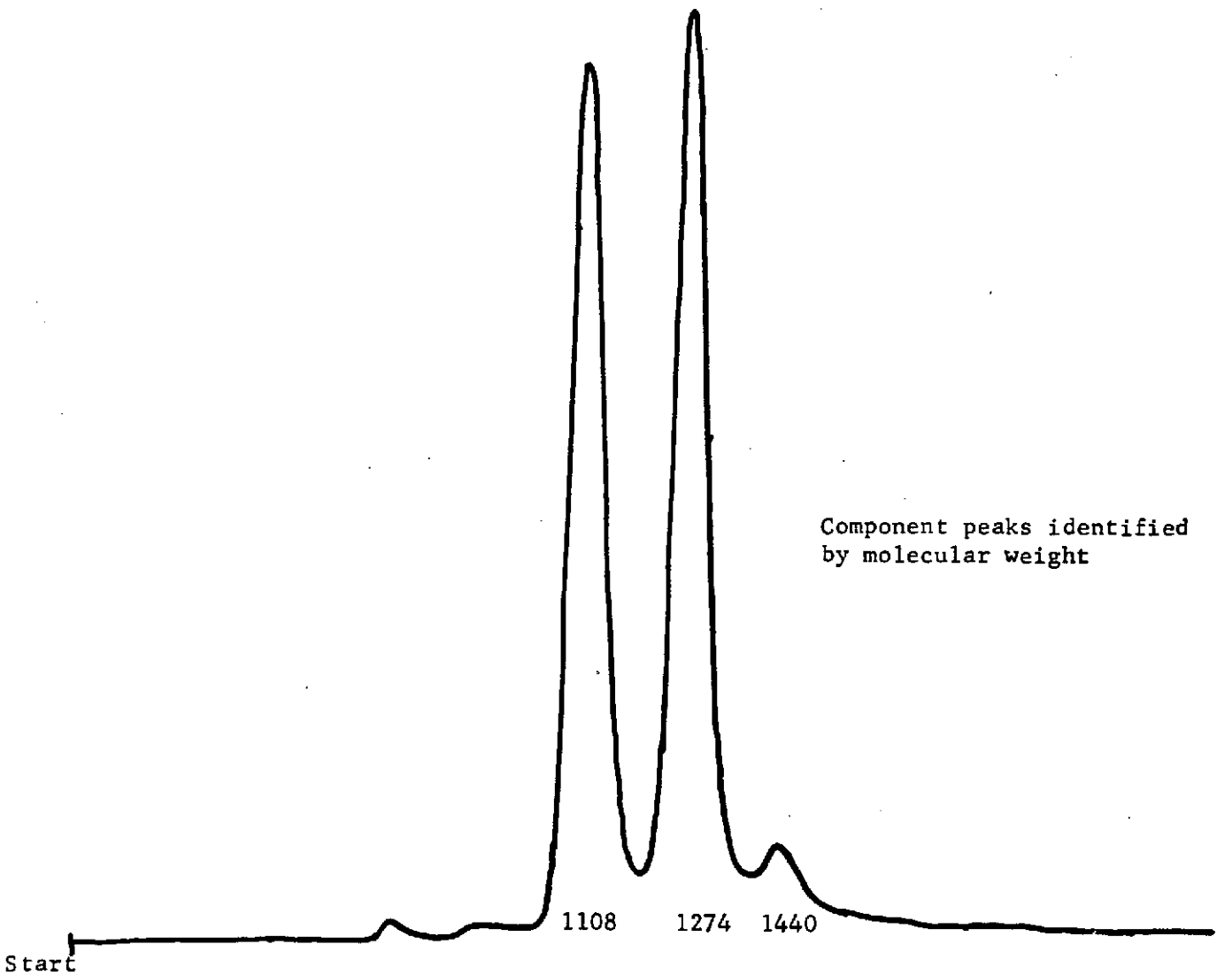


Figure 9. Gas Liquid Chromatograph of Difunctional PFPOH
Silicone rubber W-98 6' column
Column temp at start 180°C
Program rate 6°/minute to 250°C