THE DEVELOPMENT OF STRUCTURAL ADHESIVE SYSTEMS SUITABLE FOR USE WITH LIQUID OXYGEN (LOX)

by

Edward S. Harrison
Walter P. Fitzgerald Jr.

SUMMARY REPORT
Covering Period 20 June 1969 to 19 April 1970

May 1970

Prepared under Contract No. NAS 8-24389
Control No. DCN 1-9-54-20052(1F)

WHITTAKER CORPORATION
Research and Development Division
3540 Aero Court
San Diego, California 92123

for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama 35812

THE DEVELOPMENT OF STRUCTURAL ADHESIVE SYSTEMS SUITABLE FOR USE WITH LIQUID OXYGEN (LOX)

by
Edward S. Harrison
Walter P. Fitzgerald Jr.

SUMMARY REPORT
Covering Period 20 June 1969 to 19 April 1970

May 1970

Prepared under Contract No. NAS 8-24389
Control No. DCN 1-9-54-20052(1F)

WHITTAKER CORPORATION
Research and Development Division
3540 Aero Court
San Diego, California 92123

for

George C. Marshall Space Flight Center
National Aeronautics and Space Administration
Marshall Space Flight Center, Alabama 35812

FOREWORD

This report was prepared by Whittaker Corporation, Research and Development Division, under Contract No. NAS 8-24389, Control No. DCN 1-9-54-20052(1F), entitled "The Development of Structural Adhesive Systems Suitable for Use with Liquid Oxygen (LOX)", for the George C. Marshall Space Flight Center of the National Aeronautics and Space Administration. The work was administered under the direction of the Propulsion and Vehicle Engineering Division, Engineering Materials Branch, with Dr. W. E. Hill acting as project officer.

The research work was conducted in WRD's laboratory by Mr. Edward S. Harrison and Dr. Walter P. Fitzgerald Jr. Also contributing to the program were Mr. Alfred H. McLeod and Mr. William D. Warner. Analytical work was carried out by Dr. William G. Stevens and Mrs. Kay Lopez.

Prepared by : E S Harrison
Edward S. Harrison

Approved by: W. P. Fitzgerald
Walter P. Fitzgerald Jr.

ABSTRACT

The efforts on this program were directed toward development of polymer systems demonstrating LOX-compatibility and nonflammability in 100% oxygen environments. Among ultimate uses of the polymer system(s) are the three major areas:

1) Adhesives;
2) Conformal Coatings;
3) Electronic Embedment Materials

A fluorinated polyurethane based on hydroxyl-terminated polyperfluoropropylene oxide and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate was developed during previous phases of the program. The purpose of this program was to suitably modify that system to allow its use and evaluation in the above areas with the concurrent goal of upgrading of elevated temperature performance capability.

The research under this phase of the program has resulted in an approximately 60% increase in the tensile shear strengths obtained throughout the useful range (-423° to ~ 150°F) of the allophanate-cured polyurethane. Conformal coatings have been successfully prepared and show great promise. Solvented spray coatings have similarly been prepared in an initial feasibility study from fluorinated solvent and high quality nonflammable finishes have been obtained.

Newer curing schemes using cyanoguanidine, melamine and cyanuric trihydrazide have resulted in a significant improvement in moderately elevated temperature performance, with no sacrifice in the nonflammability characteristics.

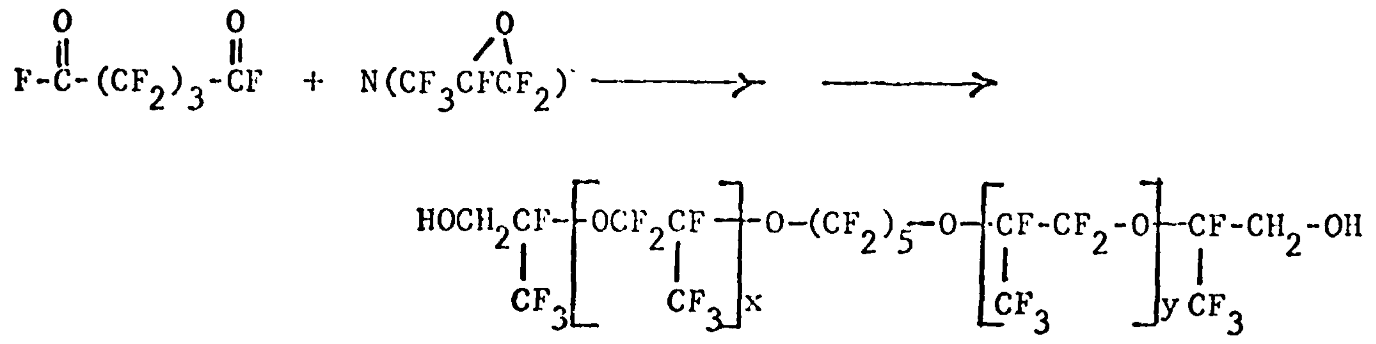
TABLE OF CONTENTS

LIST OF FIGURES

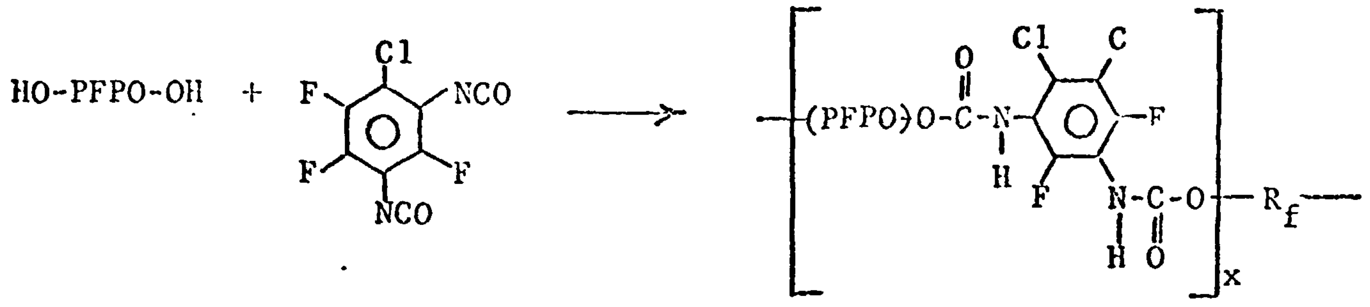
LIST OF TABLES

INTRODUCTION AND OBJECTIVES

In previous studies under Contract No. NAS 8-11068 (July 1963 to December 1968), Whittaker Research and Development Division (WRD) developed a fluorinated urethane adhesive which is suitable for use with liquid oxygen. This adhesive system based on 4-chloro-2,5,6-trifluoro-1,3-phenylene diisocyanate (ClTFPDI) and the diol of poly(perfluoropropylene oxide) initiated with perfluoroglutaryl fluoride (PFPO diol).

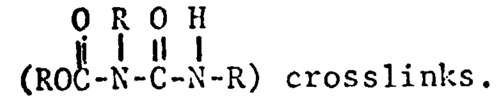


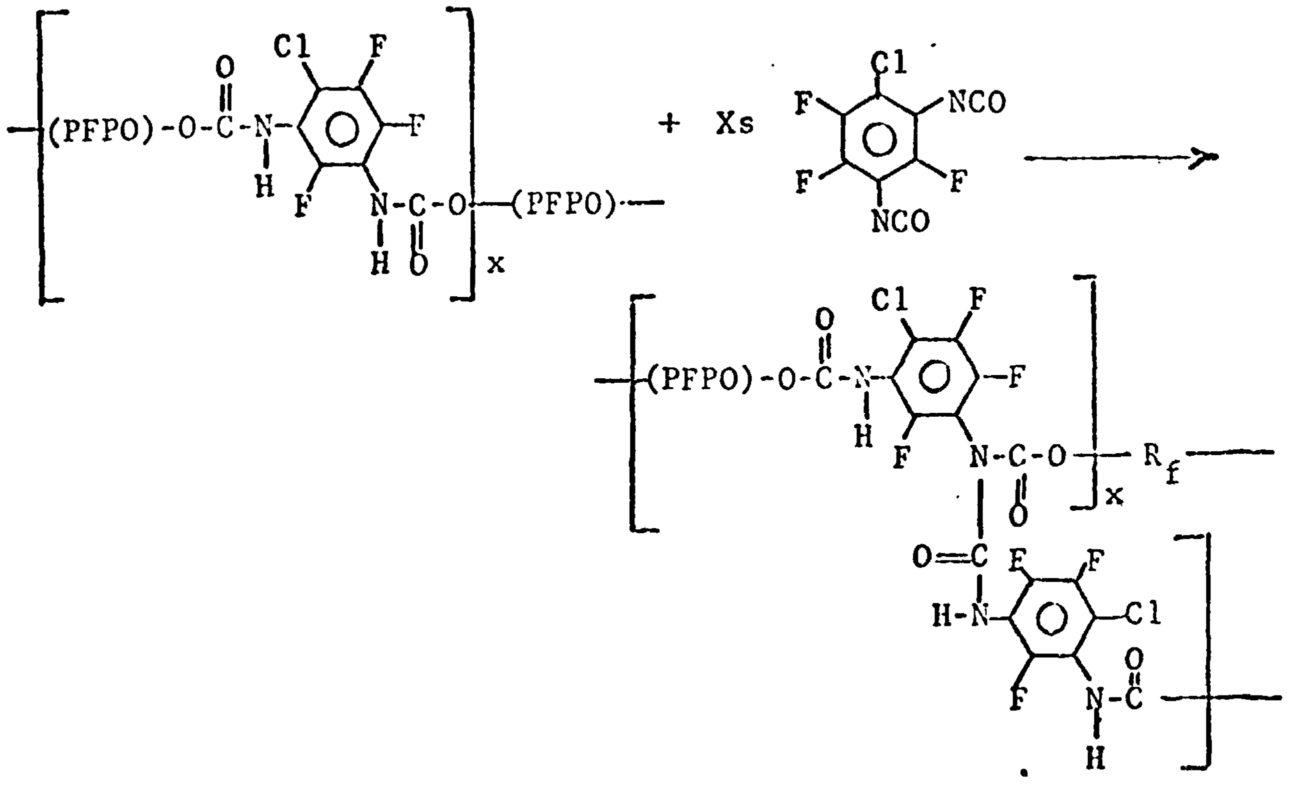
PFPO diol (x + y + 2 = N)



Linear fluorinated polyurethane

It was found that the system had optimum properties with an NCO to OH ratio of 1.8, which results in a cured polymer through allophanate


$(\mathrm{RO\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-R})$ crosslinks.



Allophanate crosslinked fluorinated polyurethane

The allophanate-crosslinked polymer system is characterized by low tear strength and very poor elevated temperature strength.

The final adhesive system developed on Contract No. NAS 8-11068 was a two-part system consisting of a ClTFPDI-capped PFPO diol prepolymer (with all the ClTFPDI added to lower the viscosity); and PFPO diol, using 0.1% ferric catalyst. This system had a low viscosity and a 5.5-hr pot life at room temperature. It cured at slightly elevated temperatures in less than one day. Typical tensile bond strengths, for this adhesive system on aluminum adherends are 5000 psi at -320°F, 1500 psi at RT and 150 psi at 200°F.

Under the present program the objectives are to improve the elevated temperature properties of the adhesive and to investigate the use of the system as a paint, conformal coating and electronic embedment compound.

DISCUSSION

I. PREPOLYMER PREPARATION AND ANALYSIS

A. Hydroxyl-terminated Polyperfluoropropylene Oxide

1. Polymerization

Continuing efforts directed toward achieving reliable and reproducible results in the polymerization of hexafluoropropylene oxide have resulted in successful, uniform large scale preparations.

The polymerization of perfluoropropylene oxide has been carried out with rigorous control of the purity and dryness of the various reactants and solvent. The cesium fluoride catalyst was oven-dried at 600°F for a total of 110 hours before use. The diglyme solvent was doubly-distilled and used immediately after distillation. All other parameters (temperatures, quantities of reactants and addition rates) were the same as utilized previously.

This initial polymerization reaction proceeded more smoothly and more cleanly than any of the previous polymerizations. After the initial polymerization is completed the final removal of cesium fluoride from the acid-fluoride terminated material is readily accomplished by filtration through very fine (VF) fritted glass funnels. We had previously encountered considerable difficulty in this step.

The reduction (Lithium Aluminum Hydride) of the acid fluoride-terminated polyether may be accomplished directly or after prior fractional distillation. In either instance, clean separation of the crude liquid product (either the unreduced acid fluoride-terminated polyether or the reduced hydroxyl-terminated polyether) into monofunctional and difunctional "envelopes" is possible by careful fractional distillation under reduced pressure.

2. End-Group Analysis and Molecular Weight Determinations

Considerable effort has been expended in establishing reliable, reproducible methods for analysis of the hydroxyl-terminated polyperfluoropropylene oxide. These data are imperative for any optimization program. Reproducibility and precision have been difficult to obtain either in our laboratories or from outside sources. Accuracy is questionable at best.

The molecular weights of the hydroxyl-terminated poly(perfluoropropylene oxide) have been determined by Vapor Pressure Osmometry using a Mechrolab Model 301A Vapor Pressure Osmometer. In this instrument the molecular weights are best determined using THF as a solvent. Other solvents investigated were Freon-TF and acetone. The instrument was calibrated using such standards as benzil, 1,5-diiodo-2,2,3,3,4,4-hexafluoropentane and 2,2',3,3,4,4-hexofluoropentane-1,5-diol. The major problems encountered in obtaining reproducible results have been the non-linearity of the ΔT versus concentration plots and the variation of the ΔT value when the concentration of the solvent is zero.

The non-linearity of the ΔT vs. Concentration plots is not a significant problem if the second problem is not manifest. The quantity, $\Delta T c$, is routinely extrapolated to zero concentration to obtain a molecular weight. The uncertainty, however, in the value of ΔT (which should be zero at zero concentration) has lent undesired ambiguity to the molecular weight data.

The normal procedure for determining the value of the molecular weight from the ΔT vs. Concentration data has been to subtract from each value of ΔT, the value of ΔT at zero concentration. This difference is then divided by the concentration and the plot ($\Delta T/c$ vs. C) extrapolated to zero concentration. The molecular weight is calculated using the following equation:

$$\text{Molecular Weight} = \frac{(\Delta T/c)\ c=0 \text{ for standard X molecular weight of standard}}{(\Delta T/c)\ c=0 \text{ for unknown}}$$

Attempts have been made to determine equivalent weights of the hydroxyl-terminated polyperfluoropropylene oxide by acetylation of the hydroxy groups and subsequent back titration of the excess acetic anhydride. Relatively good precision was obtained using this method when the acetylation was allowed to proceed for one week on a steam bath. Less precise results were obtained when shorter acetylation times were employed. Periodic attempts have been made to perform this acetylation reaction in sealed ampoules at temperatures in excess of 120°C. Ampoule failure has precluded evaluation of this technique thus far.

It has been found that one of the OH end groups of the hydroxyl-terminated polyperfluoroether can be determined by titration in acetone solvent using tetrabutylammonium hydroxide in methanol as a titrant. The method used involved a photometric titration using the absorption of azo violet at 650 mμ to detect the equivalence point. Unfortunately no convenient direct method has been found to determine the relative functionality of these materials (i.e., an hydroxyl equivalent weight). It was felt that a simple titration of an acetone solution of the hydrox erminated polyperfluoroether with the more nucleophilic potassium meth e would yield a rapid and convenient method for the determination of OH equivalent weight of these materials, and, therefore, their relative functionality. It was also felt that reliable detection of the equivalence point of this titration must be by way of an instrumental determination. This belief is based on the results observed in the above-mentioned titration studies. In this titration, reproducible results could be obtained only when a photometric procedure was used, as the visual end point is not distinct enough for reliable determinations.

The first attempt to detect the equivalent point in the titration of an acetone solution of the model diol hexafluoropentanediol, using potassium methoxide in methanol yielded a titration curve with no detectable breaks. Consequently we tried to detect the equivalent point in the titration of the same model diol, hexafluoropentanediol, using a conductivity cell. This technique was not effective. Thermometric titration of hexafluoropentanediol was attempted in a Dewar flask using a thermister-bead detector. Negative results were obtained by this procedure also.

The importance of a reliable and accurate hydroxyl number is quite apparent when one considers the wide variations in properties of cured polyurethane which may be obtained by simple variations in the molecular weight of the hydroxyl-terminated poly(perfluoropropylene oxide). The major concern is, of course, the actual degree of functionality. Ideally, only difunctional material would be utilized in any polymer formulation; hence, a much greater degree of confidence has been required in the hydroxyl number than is presently obtainable.

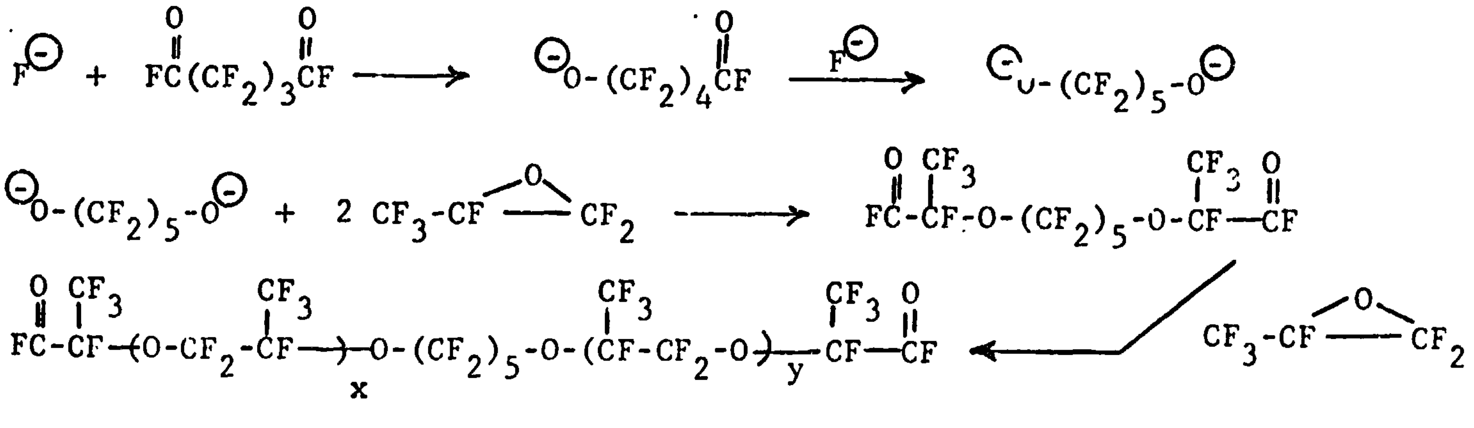
The dual problem of molecular weight determination and hydroxyl functionality has been most satisfactorily solved recently by utilizing Vapor Phase Chromatography for molecular weight distribution analysis, as described below.

3. Vapor-Phase Chromatographic Analysis

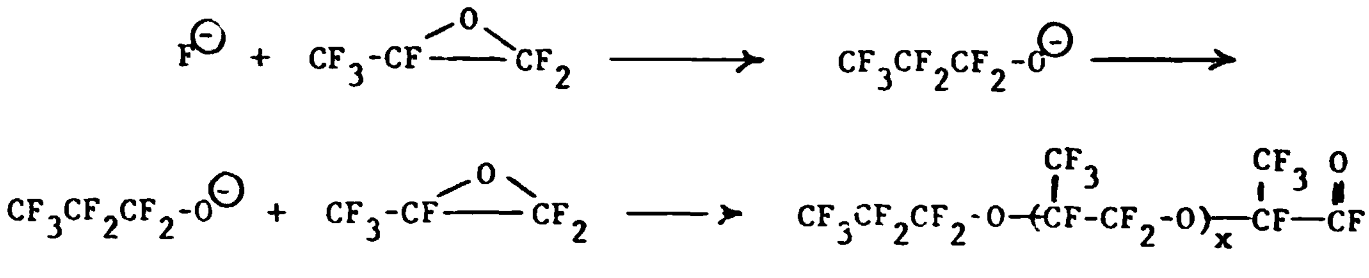
Resolution of the complex mixture of hydroxyl-terminated PFPO has been accomplished by the Vapor Phase Chromatographic Analysis. The peak separation is not perfectly clean but is very adequate to provide us with reliable molecular weight estimation. A large number of different temperatures, programmed temperature increase rates, flow rates, etc., were studied before the right combination of conditions was developed.

Chromatograms of the crude product from the lithium aluminum hydride-reduction of acylfluoride-terminated polyperfluoropropylene oxide have demonstrated a quite clear separation into two separate "envelopes" of monofunctional and difunctional material.

As mentioned previously, the polymerization of perfluoropropylene oxide is carried out in diglyme solvent using perfluoroglutaryl fluoride as initiator and cesium fluoride as catalyst as follows:



Monofunctional material arises from an initial ring opening reaction by fluoride ion, e.g.:



In our experience this undesired ring opening can be suppressed to a marked degree by carefully controlling the temperature during the initial phases of the polymerization.

Fractionation of crude acyl fluoride-terminated material results in excellent separation of low molecular weight difunctional and all monofunctional material from the desired higher molecular weight difunctional telomers.

As discussed previously, considerable ambiguity was present in both end group analysis and molecular weight (as determined by VPO) of hydroxyl-terminated prepolymer. The acyl fluoride-terminated material on the other hand gives excellent straight line VPO plots, consistently intersecting at $\Delta R/c=0$ at zero concentrations. End group analysis is accomplished by simple titration with aqueous base. This method yields rapid, accurate and precise values.

Work on a related NASA contract gave the following analytical results for acyl fluoride-terminated polyperpropylene oxide:

Mol. Wt. (by VPO in Freon 113)	Acid Fluoride Number	Degree of Functionality
1360 ±10	681, 680, 680	2.00

An alternate study, using vapor phase chromatography, was undertaken, concurrent with those intensive investigations on analytical procedures, aimed at thorough analysis of the <u>hydroxyl</u> terminated perfluoropolyether.

Fractional vacuum distillation of the mixture was carried out on a Nestor-Faust Spinning Band Column. Separation was quite tedious but resulted in the isolation of fractions of sufficient purity to permit identification of the component peaks of the mixture.

The VPC chromatograms are shown in the following figures. Identification of the materials in those fractions was accomplished using the following rationale:

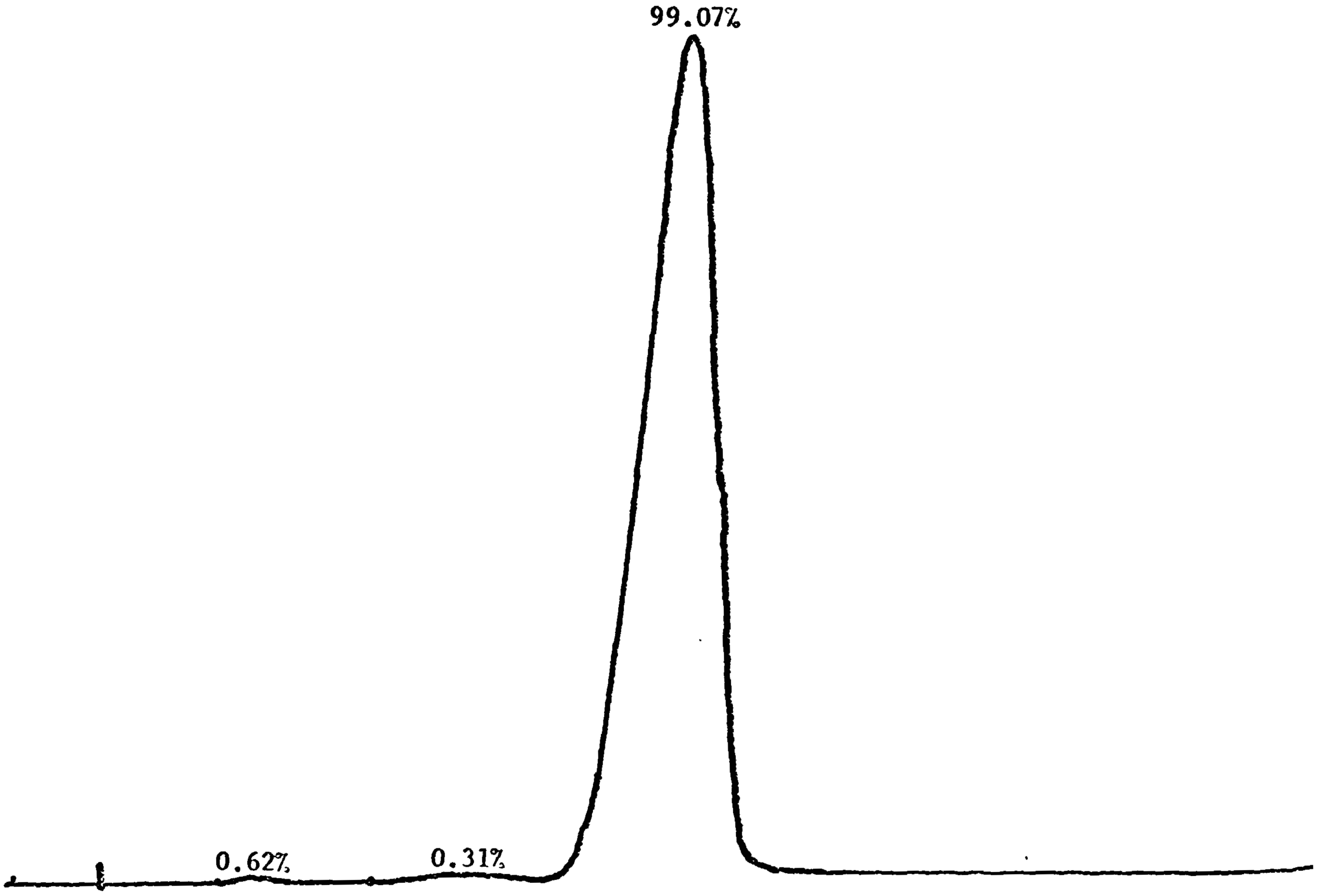


Figure 1. VPC Chromatogram of PFPO, Cut 2

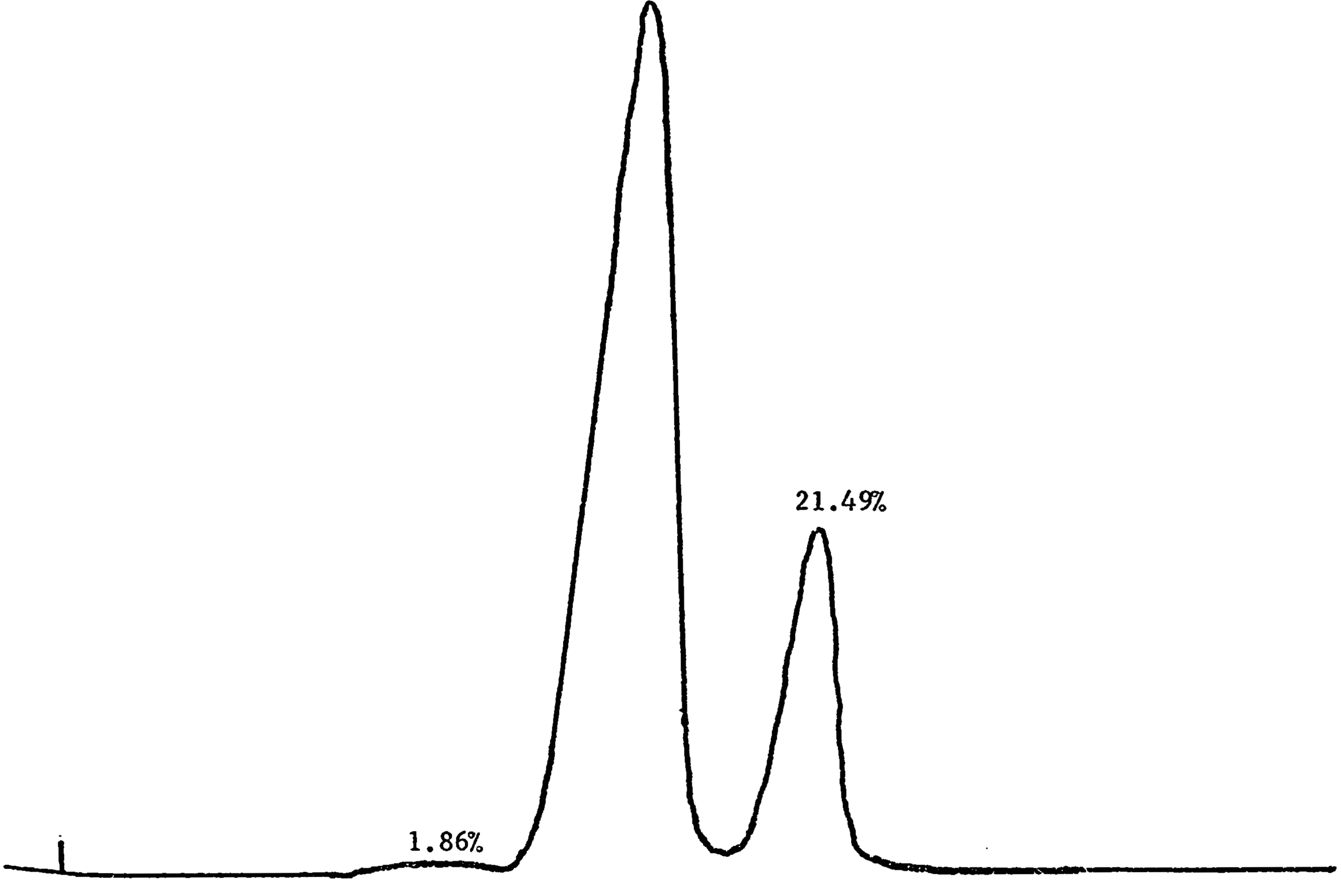


Figure 2. VPC Chromatogram of PFPO, Cut 3

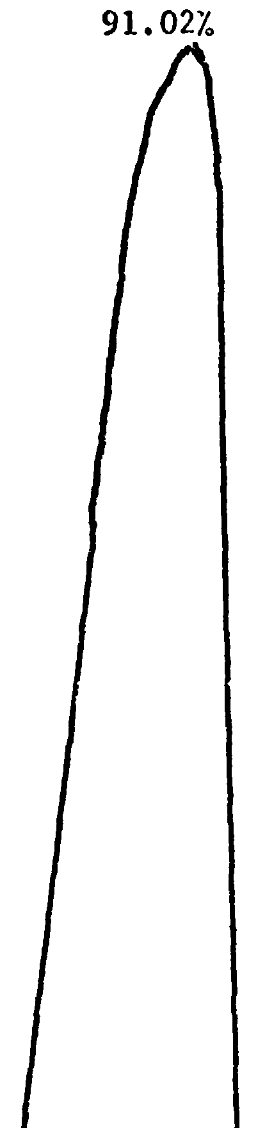
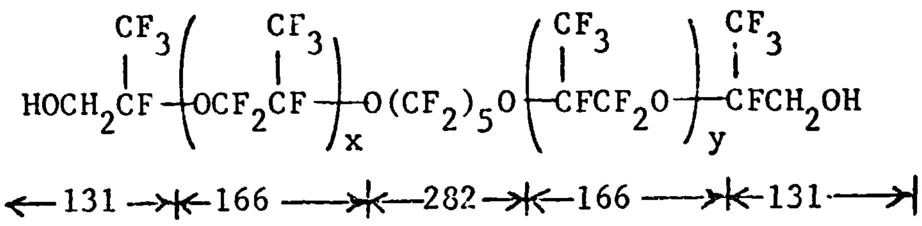


Figure 3. VPC Chromatogram of PFPO,
Cut 4

1) The structure of the prepolymer is such that it can only vary by an ordered increment. In other words, the molecular weight difference between the various telomers must be precisely 166 (the molecular weight of the hexafluoropropylene oxide monomer repeating unit: x and y)



$HOCH_2CF(CF_3)\left(OCF_2CF(CF_3)\right)_xO(CF_2)_5O\left(CF(CF_3)CF_2O\right)_yCF(CF_3)CH_2OH$

2) It is presumed that, in the higher molecular weight fractions, the retention times and boiling points of the various isomers of a given molecular weight will be essentially identical. That is, the x=1 and y=4 isomer will have essentially the same b.p. and retention time as x=2 and y=3.

3) The peak areas truly represent mole fractions. The molecular weights of the various components must vary in the following order:

(x + y)	mol.wt.
2	876
3	1042
4	1208
5	1374
6	1540
7	1706
8	1872

The molecular weights of the isolated fractions shown in the figures were independently determined by vapor pressure osmometry in THF solvent.

Cut#2 was found to have a molecular weight of 1339. If the major peak (99.07%) is assigned to be the telomer where (x+y) = 5 (m.w. = 1374), and the two lower boiling (shorter retention times) peaks to fractions of (x+y)=4 (0.31%) and 3 (0.62%), respectively, then the calculated molecular weight is 1371.

Cut #3 contains 76.63% (x+y)=5 telomer plus 1.86% (x+y) = 4 and 21.49% (x+y)=6. The molecular weight by VPO was found to be 1360. The calculated molecular weight is 1406.

Cut #4 contains 91.02% (x+y)=6 plus 8.98% (x+y)=7. The molecular weight by VPO was found to be 1530. Calculation results in a value of 1555.

The excellent correlation of these results substantiates the rationale and will allow a faster, more precise estimate of molecular weights for PFPO prepared subsequently, without resort to the less satisfactory incumbent VPO procedure.

It should be noted that the VPO values are consistently low. Also it appears that the more complex mixtures of PFPO produce the more pronounced departures from ideality in the VPO plot of ΔR (or $\Delta R/c$) vs. C. This certainly tends to reduce the confidence level in the molecular weight data by this method. The VPO plots of the relatively pure fractions are, on the other hand, quite good. Essentially linear plots with extrapolated zero intersection was the rule in these cases.

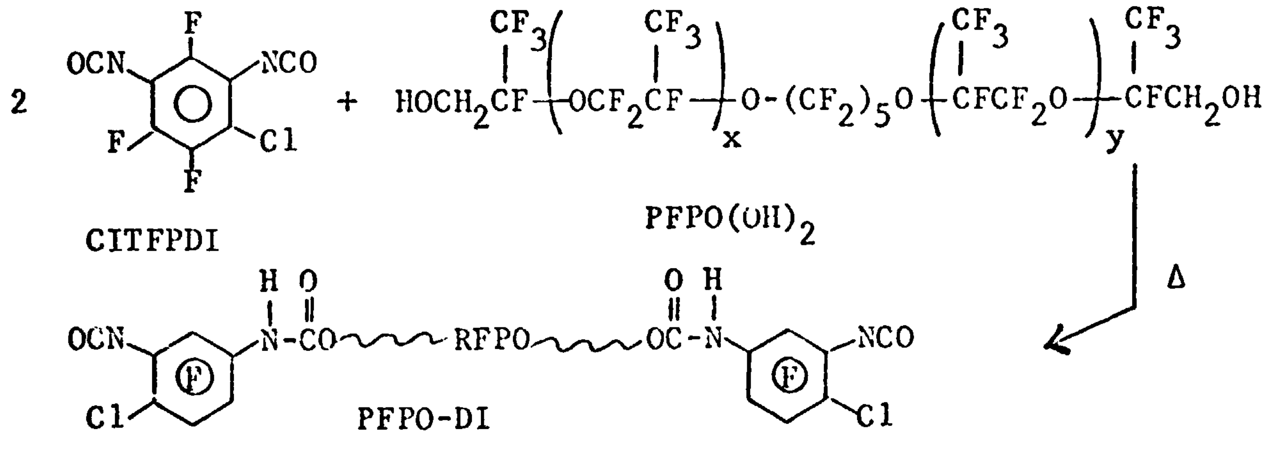
II. ADHESIVE SYSTEMS

A. Allophanate-Cured Systems

1. Prepolymers

A major disadvantage of the derived highly fluorinated polyurethane system lies in the almost complete mutual immiscibility of the hydroxyl-terminated polyether (ClTFPDI) and 4-chloro-2,5,6-trifluoro-m-phenylene diisocyanate at temperatures below 80°C.

Prior work led to the development of methods for termination (end capping) of the PFPO with ClTDPDI.

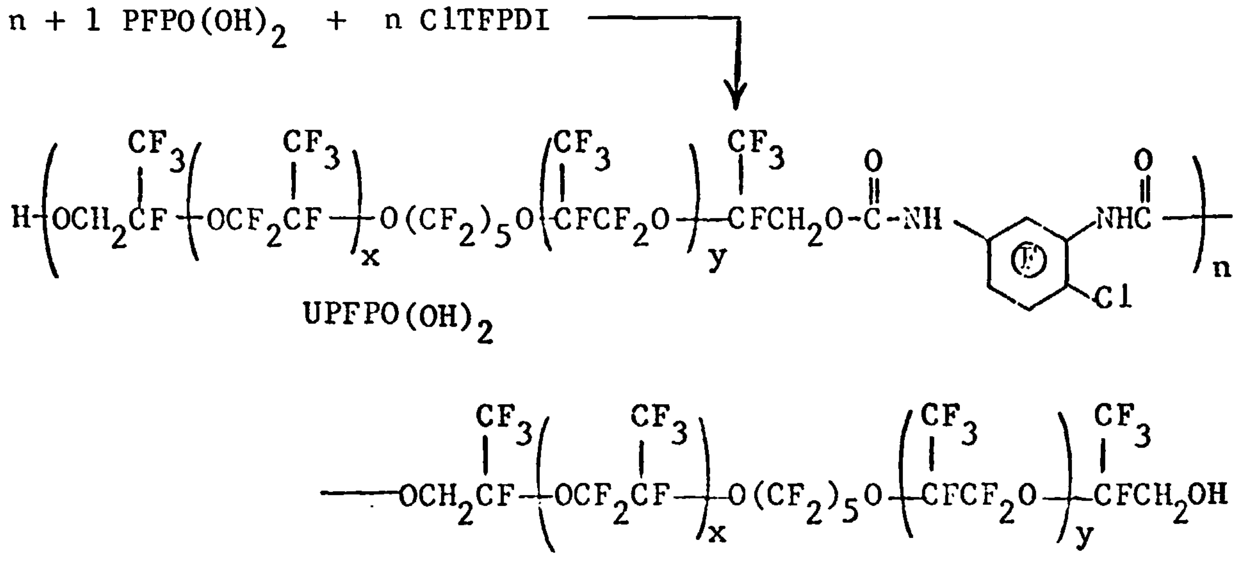


The "capping" of hydroxyl-terminated polyperfluoropropylene oxide PFPO(OH)$_2$ with 4-chloro-3,5,6-trifluoro-m-phenylene diisocyanate (ClTFPDI) to produce the derived isocyanate-terminated prepolymer (PFPO-DI) has been repeatedly carried out with facile reproducibility. PFPO-DI seems to be quite stable when stored in a dessicator at ~ 5°C. No significant change in viscosity has been noted after up to 6 weeks storage under these conditions.

2. Adhesive Formulation

It had been anticipated that subsequent admixture of the PFPO-DI with additional ClTFPDI and PFPO(OH)2 would result in a truly homogeneous prepolymer mixture. This expectation was not, however, realized. The mixture was quite fluid but not homogeneous, as evidenced by a milky appearance. Initially we felt this non-homogeneity was probably due to the stannous octoate catalyst. The same milky appearance, however, was observed in the absence of catalyst. While adequate bond strengths (at <150°F) can be obtained with this system it was felt that even better properties could result if a homogeneous system could be developed.

We directed our efforts toward achieving this goal by preparing the "reverse" capped urethane-extended, hydroxyl-terminated, prepolymer [UPFPO(OH)2] (cf. below).



UPFPO(OH)$_2$

This prepolymer has been routinely prepared several times with reproducible results.

Table I lists the bond strengths obtained when the overall NCO/OH ratio was systematically varied from 1.8/1 to 1/1. This NCO/OH ratio includes that quantity exhausted in the formation of the original prepolymers, PFPODI and UPFPO(OH)2. The prepolymer mixtures were always degassed prior to adhesive application and in all cases, became crystal clear after the deaeration process.

TABLE I

ALLOPHANATE CURED SYSTEMS
PFPO-DI + UPFPO(OH)$_2$
PFPO(OH)$_2$, 1550 Molecular Weight

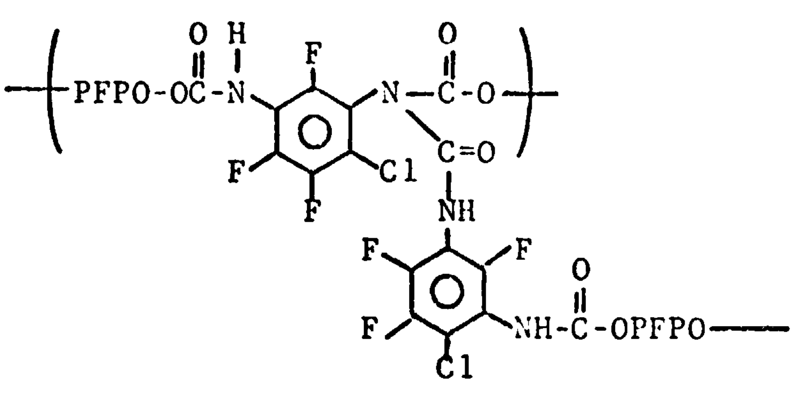
Overall NCO/OH	Avg Tensile Shear, psi at -320°F	Avg Tensile Shear, psi at 77°F	Avg Tensile Shear, psi at 200°F
1.8/1	7300	2325	296
1.6/1	7240	2245	326
1.5/1	7880	2165	321
1.4/1	7410	1845	211
1.3/1	--	1390	--
1.2/1	--	1200	--
1.1/1	--	372	--
1/1	--	37	--

The handling characteristics of the various systems were uniformly excellent. Easily spreadable, homogeneous systems of moderate viscosity were the general rule. The failed specimens were essentially bubble-free and exhibited almost exclusively adhesive failure. The exposed metal surface was essentially free of any polymer.

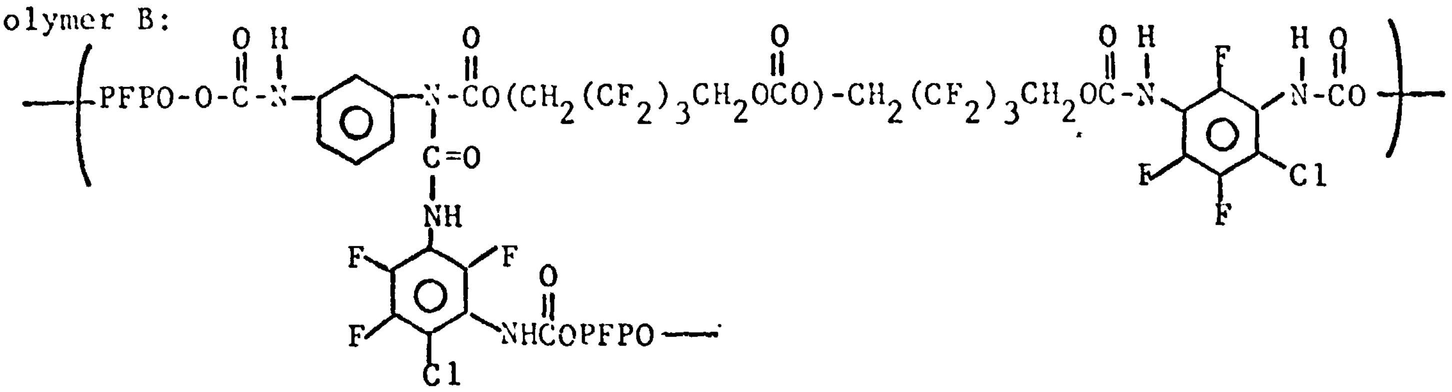
An alternate allophanate-cured system was investigated, based on a block copolymer approach.

A hydroxyl-terminated, highly fluorinated polycarbonate of hexafluoropentanediol was prepared (mol. wt. 715) and co-polymerized with PFPODI (in excess). The normal system [UPFPO(OH)$_2$/PFPODI] is shown below as Polymer A, with the crosslinked block co-polymer designated as Polymer B.

Polymer A:



Polymer B:



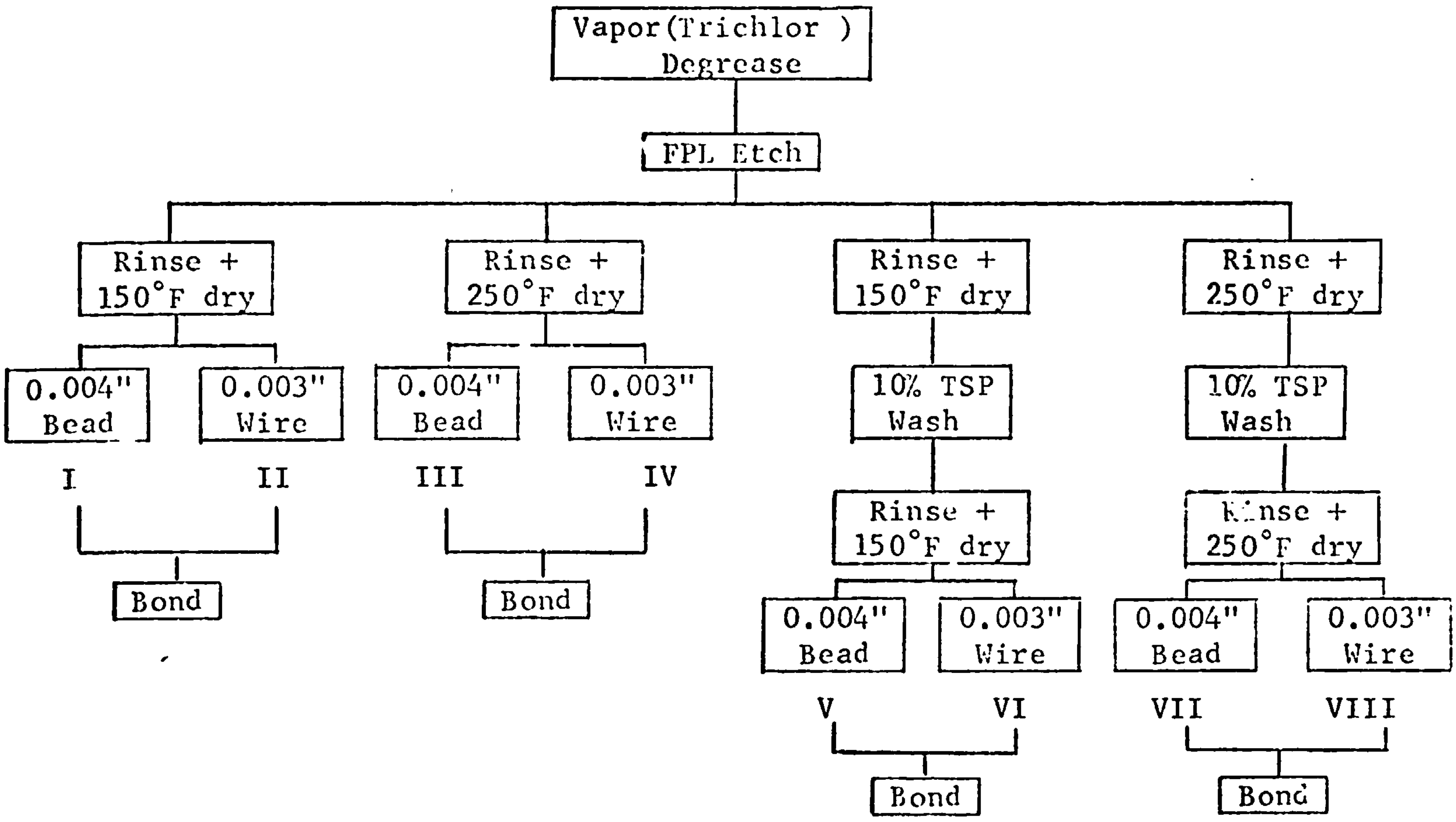
Since both of these systems are cured by an allophanate-crosslink mechanism, the 200°F properties are not expected to be appreciably different. The room temperature properties of the mixed polycarbonate/polyether urethane, however, appear to be somewhat improved over those of the straight polyether urethane. The pressed film exhibited improved tear strength and toughness and also was much more elastomeric. LOX-compatibility tests were not run, but flammability in ca. 100% oxygen atmosphere (WRD test) for both systems were essentially identical. They were both rapidly self-extinguishing when ignited with an oxygen/gas torch.

B. Bonding Surface Preparation

1. Metal Conditioning

The appearance of an excessive amount of bubbles in the bond lines of failed adhesive specimens prompted an investigation directed toward uncovering their source. It was presupposed that the bubbles were due primarily to adsorbed moisture on the metal surface. A series of tensile shear specimens were prepared. The surface preparations (prior to bonding) followed the outline shown below.

Scheme I.
Variations in Bonding Procedure



Tensile shear values and observations are shown in Table II. The overall NCO/OH ratio was 1.8/1.

TABLE II

EFFECTS OF BONDING PREPARATION ON ADHESIVE PROPERTIES

Specimen Preparation Code*	Tensile Shear, psi (Avg) -320°F	77°F	+200°F
I	6080	2415	296
II	7320	2330	288
III	5370	2295	270
IV	7420	2230	210
V	5260	2110	162
VI	4940	1990	164
VII	4940	2020	208
VIII	5400	1860	258

* cf. Previous Scheme I.

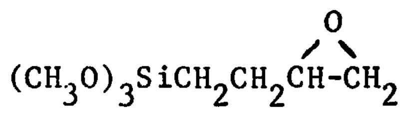
Those specimens prepared using 0.004 in. glass beads as spacers showed a significantly greater amount of bubbles, than those utilizing the 0.003 in. wire. The 250°F drying cycles proved to be somewhat disadvantageous, as compared to the standard 150°F drying cycle. Trisodium phosphate-wash likewise produced a detrimental effect. We have, therefore, decided to use the wire shims and 150°F drying for adhesive specimen preparation in future testing applications. The failed bond lines of this system are essentially bubble-free but indicate almost 100% adhesive failure.

2. Primer Study

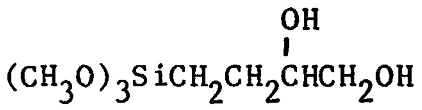
In an effort to upgrade the adhesive performance of this allophanate cured system, a number of primer candidates were studied. These primers included Dow Corning's Z-6020, Z-6040 and Z-6040 (hydrolyzed). The efficiency of these primers has been well established on non-fluorinated polyether urethane adhesive systems. The improved fluorourethane system yielded, however, discouraging strength results (at a 1.8/1 NCO/OH ratio) when these metal primers were utilized. All three primers were applied by a spray technique and dried per the manufacturer's instructions. The tensile shear strengths are tabulated in Table III. The Z-6040 did show slight improvement in 200°F strength but the increase was not of sufficient magnitude to warrant further investigation.

$(CH_3O)_3SiCH_2CH_2CH_2NH_2$

Z-6020


$(CH_3O)_3SiCH_2CH_2CH\text{-}CH_2$ (with O bridging CH and CH_2)

Z-6040


$(CH_3O)_3SiCH_2CH_2CH(OH)CH_2OH$

Z-6040 (hydrolyzed)

TABLE III

EFFECT OF METAL PRIMERS ON ADHESIVE STRENGTHS

Primer	Avg Tensile Shear, psi at 77°F	Avg Tensile Shear, psi at 200°F
Nil	2570	326
Z-6020	1190	259
Z-6040	2300	406
Z-6040 (hydrolyzed)	1950	264

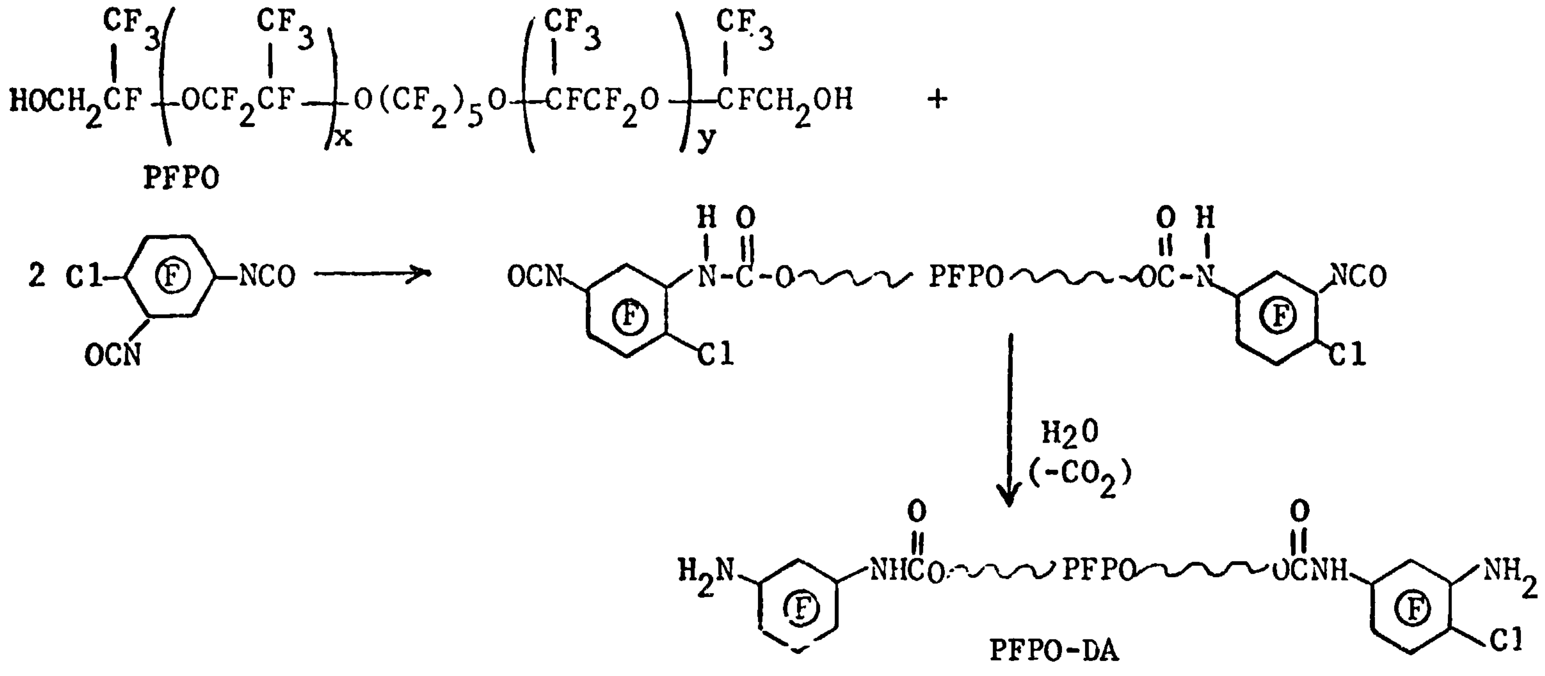
Bond failure was again essentially 100% adhesive in nature.

III. ALTERNATE CURING AGENTS

A. Amine-Terminated PFPO (PFPO-DA)

1. Amine-Terminated PFPO

Previous reports have described in detail the preparation of an amine-terminated perfluoropolyether prepolymer. The preparation has been accomplished as follows:



Hydroxyl-terminated polyether of 934 molecular weight was utilized in this preparation. The resulting amine-terminated material had a molecular weight of 1734, indicating approximately 20% chain extension during the hydrolysis step. It was obtained as a semisolid at room temperature.

The extended prepolymer system was prepared by reacting the diisocyanate-terminated polyether with the amine-terminated derivative in the ratio of 1.8/1, using stannous octoate as catalyst. Aluminum panels were coated with the viscous polymer premix. Tensile shear bonds were also prepared from this formulation. The flow characteristics of the premix material were thusfar only marginal. The resulting films were hard, tough and had a high gloss after a cure of 16 hours at 160°F, with a postcure of 8 hours at 250°F.

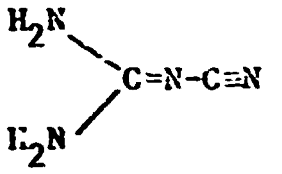
Tensile shear strengths from the above system were, however, dramatically improved, and these values are tabulated below:

Test Temp, °F	Tensile Shear Strength, psi (Average)
-320	3120
75	3670
+200	532
+330	24

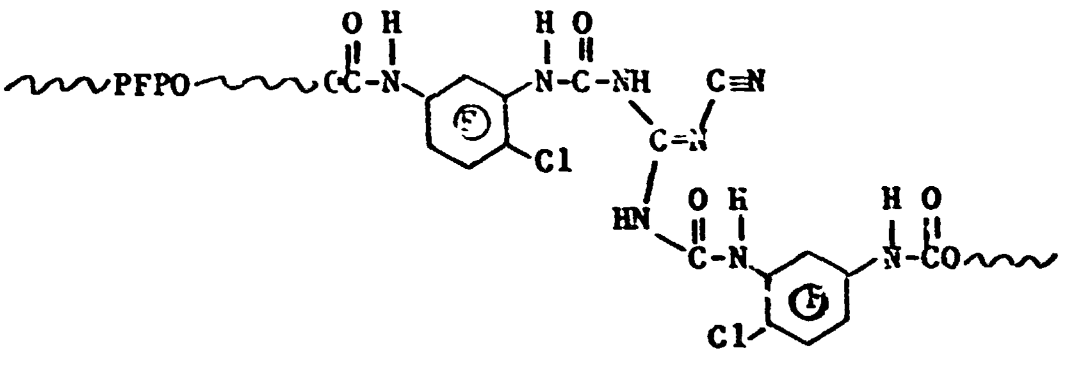
While the higher-temperature strengths still required further improvement, this system nevertheless, represents a more processible system with extended upper temperature capability over the present polyurethane system.

B. Cyanoguanidine Curing Agent

A brief study has been made using cyanoguanidine as a curing agent for the same diisocyanate-terminated prepolymer itself, prepared above in this initial adhesive formulation.


Cyanoguanidine

We chose this reagent as a candidate curing agent since it possesses no carbon-hydrogen bonds and would consequently not be expected to impart flammability to the final polymer. A second consideration for its use is the high density of polar groups provided at the chain extending sites, in the proposed reaction mechanism:


Proposed Cyanoguanidine Chain-Extension

Differential scanning calorimetry (at 5°C/min) of this system showed a reaction occurring at 135°C and a plateau at 165°C. Cure of the adhesive system was carried out at 150°C and 5 psi. The ratio of isocyanate-terminated PFPO to cyanoguanidine was 1:1 (assuming difunctionality of the curing agent), to produce essentially linear polymer. No metal salt catalysis was employed.

The prepolymer mix proved to be quite fluid at cure temperature and the bonded area of the tested coupons showed a high percentage of "starved" area. Bond strengths are listed below and reflect this deficiency.

Temperature	Tensile Shear, psi Average of Two Determinations
75°F	1575
200°F	408
330°F	25

Subsequent studies indicated that cyanoguanidine does not behave simply as a difunctional amine when the cure is carried out at 350°F. Samples cured with different cyanoguanidine concentrations at 250°F and 350°F show a marked difference in appearance and properties. Those materials cured at the lower temperature (even for prolonged periods, > 24 hours) showed considerable amounts of residual unreacted curing agent. Those cured at 350°F were clear and transparent.

Infrared analysis of cured films showed the characteristic doublet of cyanoguanidine at 2175 and 2210 cm^{-1} in those specimens which received the 250°F cure. Those which had the 350°F cure showed no peak in the nitrile region.

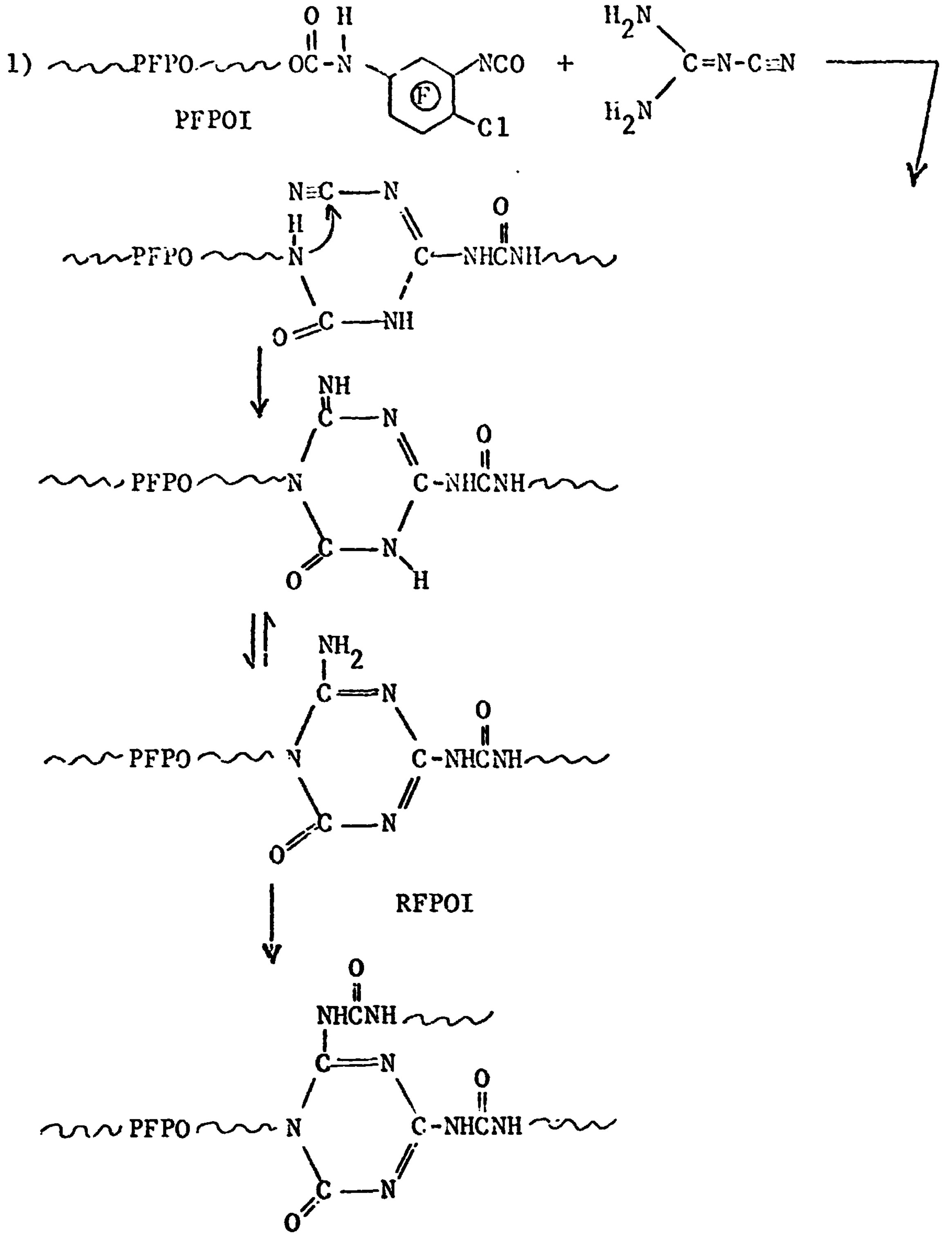
Cursory inspection of the several cured films indicated an apparent maximum in toughness can be obtained from reactions carried out with a ca. 3/2 stoichiometry. Adhesive bonds were prepared using molar ratio of 3/1.8. Cure was one hour at 350°F.

The lap shear strengths are shown below. The Durometer readings on the cured resin were 94 (Shore A-2) and 50 (Shore D). The marked improvement in elevated temperature strengths is most encouraging.

Temperature, °F	Lap Shear (psi) (Avg)
77	2565
180	995
250	676

Probably the most plausible explanation for the apparent "trifunctionality" of cyanoguanidine and the corresponding disappearance of the nitrile peak with a 350°F cure can be illustrated by the following proposed reaction scheme.

Scheme II.
Proposed Cyanoguanidine Curing Mechanism



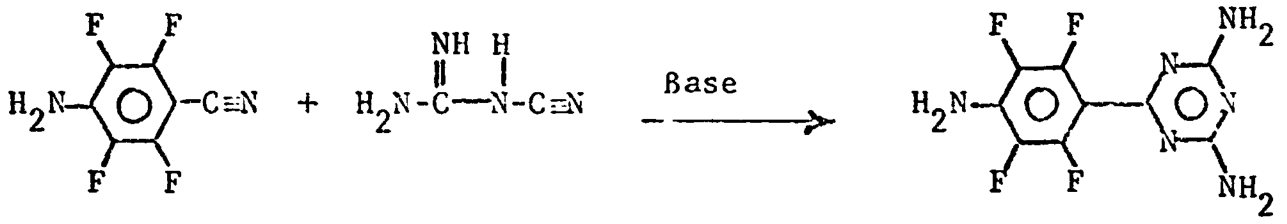
This tentative proposed cure mechanism is consistent with the known reactions of cyanoguanidine, and with the spectral properties displayed by the film samples.

The material which was cured at 250°F and in which residual unreacted cyanoguanidine was apparent, was found to be flammable in a ca. 100% oxygen atmosphere screening test performed at WRD. The fully cured material was immediately self-extinguishing upon removal of the gas/oxygen torch flame.

The experiments were repeated using both stannous octoate and triethylamine as catalysts. In both instances the mixture gelled almost immediately after admixture of the catalyst.

C. Tetrafluoro-p-amino Benzoguanamine Curing Agent

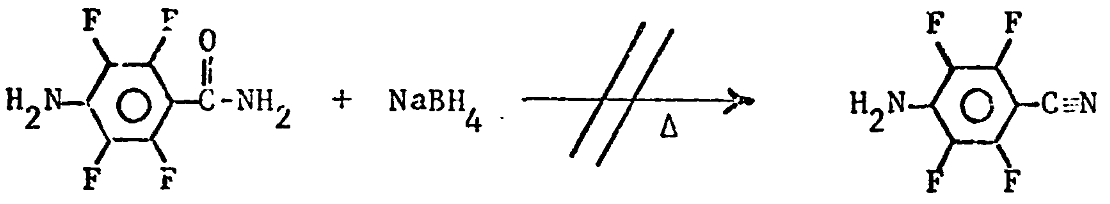
To prepare an alternate trifunctional extendor/crosslinking agent, effort has also been directed toward synthesis of tetrafluoro-p-cyano aniline (I). This compound was intended for use in the synthesis of a new curing agent by reaction with cyanoguanidine to yield the trifunctional amine, tetrafluoro-p-amino benzoguanamine (II).



(I) (II)

It was hoped that II would be an effective curing agent for the fluorinated polyurethane system. The cured polyurea-urethane should also possess improved high-temperature properties and oxygen nonflammability.

Synthesis efforts were limited to the attempted dehydration with sodium borohydride of the commercially-available p-aminotetrafluorobenzamide.



The reaction was run under three different reaction conditions, but none of the desired product was obtained in any case. This reaction is known to proceed normally with the nonfluorinated analogue.

Further synthetic efforts were precluded since it was felt that extended synthetic work would detract from other more promising studies cited above and below.

D. Substituted Triazines

It has been an objective of this program to improve the crosslinking bond strength and efficiency of the LOX-compatible and oxygen nonflammable poly(perfluoropropylene oxide) (PFPO) urethane system, to provide additional strength and thermal stability while maintaining desirable fluidity for conformal coatings and electronic embedment utilization, as well as for adhesive applications. Our method has been to utilize the formation of cyanurate urea (or semicarbazide) linkages, formed by chain extension of the isocyanate-capped PFPO bis-urethane prepolymer by reaction with melamine, cyanuric trihydrazine or a prepolymer derived from either of these structures. Such extension linkages have demonstrated thermal stability and facility of curing at 170°-250°F, and offer promise of upgrading the end-properties of the fluorinated polyurethane. We have aimed at modifying the polyurethane to a minimum degree to retain ease of fluid processing in the above-mentioned application areas. This requirement demands that the crosslinking be highly efficient at low crosslink density.

We have demonstrated that the cyanuric trihydrazine-extended, cyanurate-semicarbazide (or cyanurate-urea) crosslinked poly(perfluoropropylene oxide) bis-urethane system, which can be utilized to give a "Y" (by 2:3 stoichiometry) or "H" (by 1:1:1 stoichiometry) cure (depicted in Figure 1 for the "Y" cure) is a very rapid (5 minutes at 200°F) curing system, producing a rather stiff elastomer in both cases. The system is not very fluid, and consequently requires rubber-mill prepolymer processing. The product was, however, oxygen nonflammable (and nonigniting) under our test conditions. Also, it was quite strong, demonstrating very well the suitability of this curing mechanism with high, or medium crosslink density.

It appears that the cumulative effect of the hydrogen-bonding in this system precludes development of desirable elastomeric properties. Recourse was, therefore, made to a less hydrogen-bonded system, with a lower crosslink density. In order to retain the cyanurate crosslink, with its enhanced stability, at lower densities, melamine was first incorporated into the PFPO bis-urethane system by a "re-capping" reaction of excess melamine with isocyanate-capped prepolymer in refluxing THF, according to Figure 2.

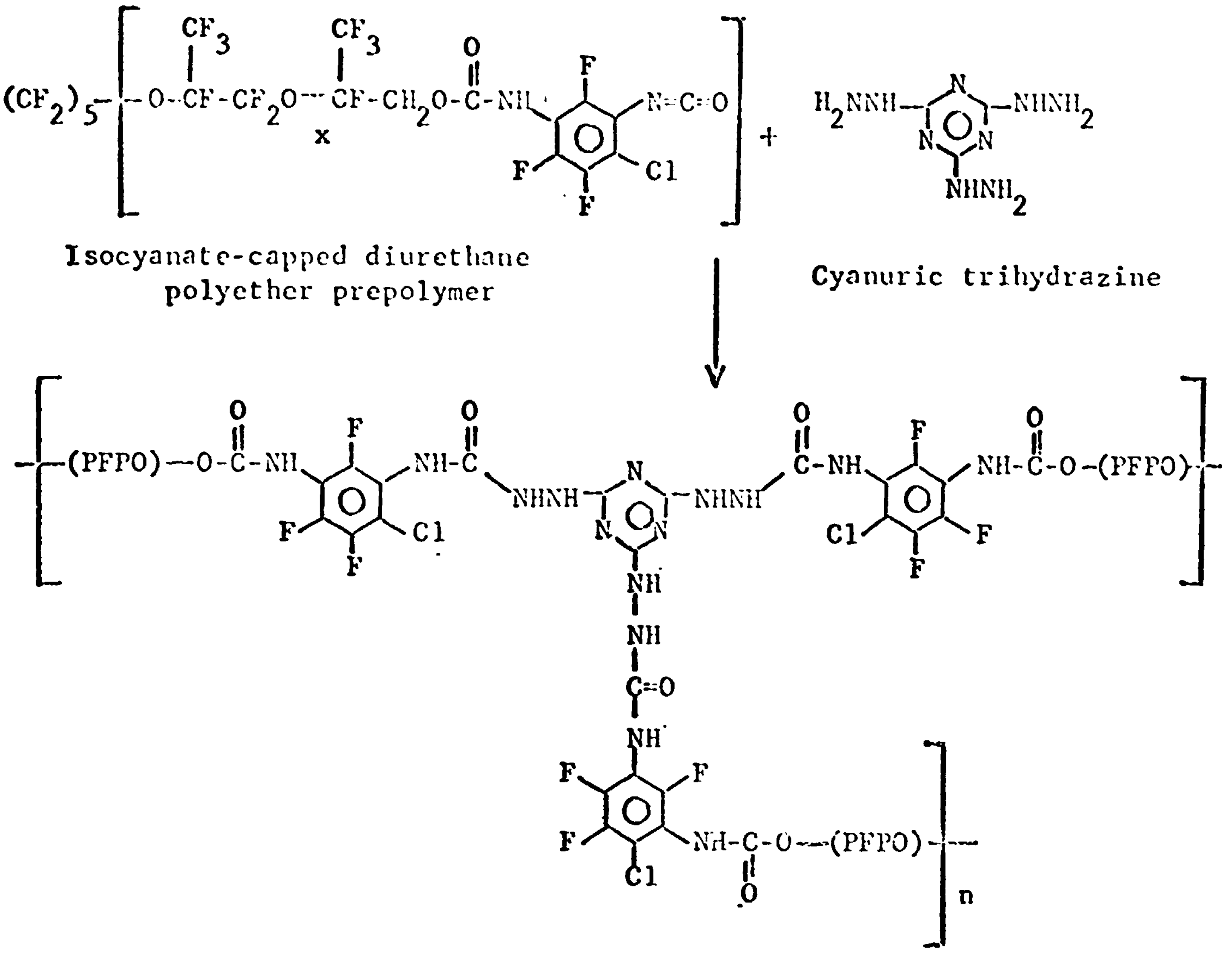


Figure 4. Cyanurate-semicarbazide extended, cyanurate-semicarbazide crosslinked poly(perfluoropolypropylene) bisurethane (Y-Crosslink)

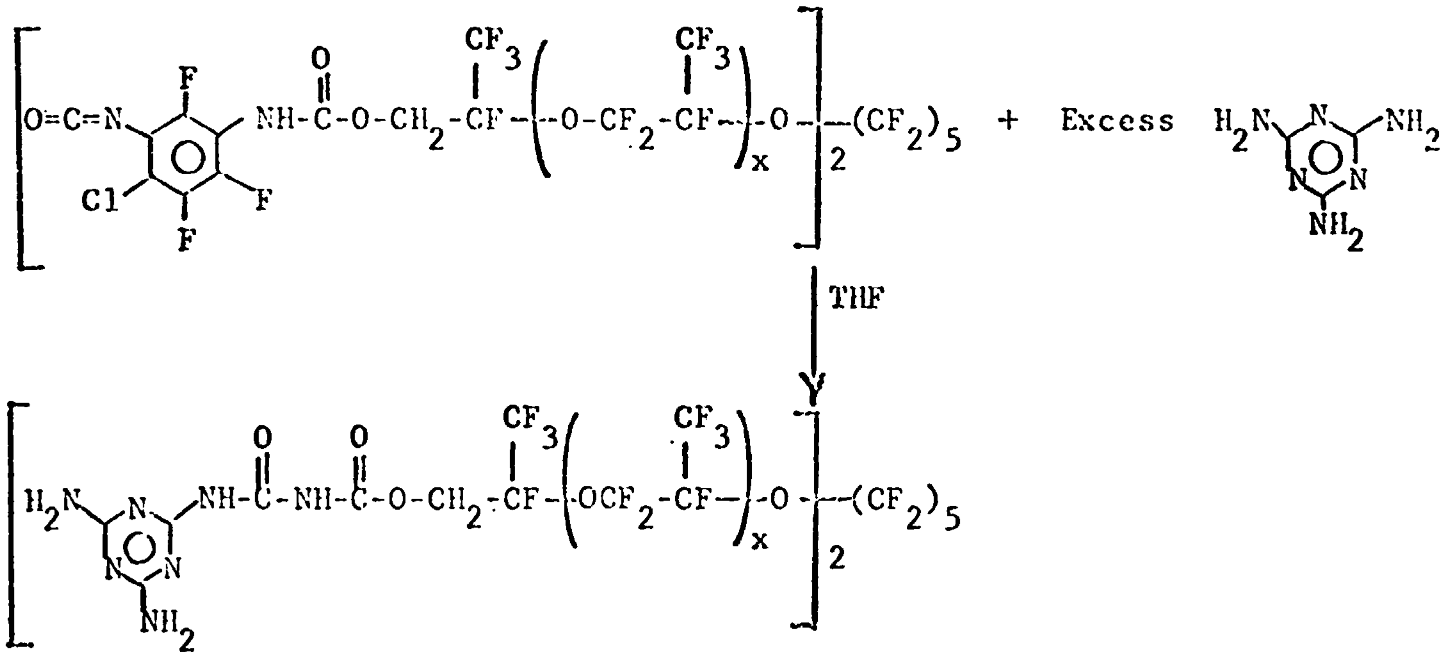


Figure 5. Melamine-capped prepolymer preparation

This structure, a glass-like solid soluble in THF, PMT ∼ 300°C, was utilized to prepare co-extended polymer systems containing melamine residues in low concentration. It was found that the recapped prepolymer was compatible in the isocyanate-capped prepolymer-glycol-terminated system, and produced transparent polymer in 1:1 incorporation reactions. Thus, by reacting the parent isocyanate-capped prepolymer with a mixture of glycol-terminated perfluoropolyether (to generate urethane) and melamine-capped prepolymer (to generate cyanurate-urea) linear extended systems, were prepared. Mixtures of glycol/melamine-capped polymer of 0.9/0.1 and 0.95/0.05 were used to generate extended polymer containing 5-mole-percent and 2.5-mole-percent melamine residues respectively. The copolymer can be represented schematically as follows (Figure 3).

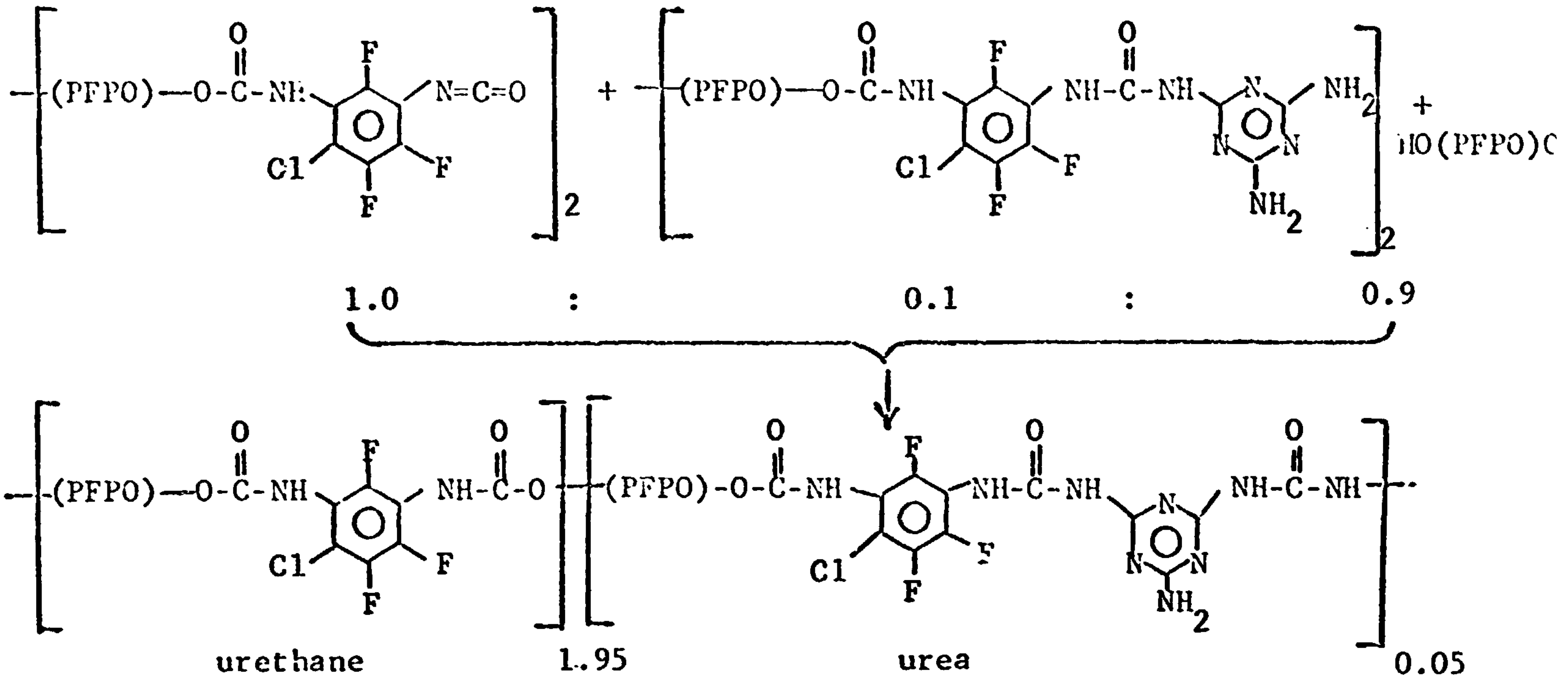


Figure 6. Cyanurate-urea copolymer preparation

These linear co-extended systems were hard, clear masses at room temperature, and melted reversibly at ca. 200°C to mobile liquids.

In order to cure these systems, chlorotrifluoro-*m*-phenylene diisocyanate was used. Initially the molar amounts of diisocyante used corresponded to the mole-percentages of the melamine incorporated in the chain extension. In both cases, this was insufficient reagent for effective curing at either 170°F or at 250°F in press cure at 2000 psi. Incremental increases in diisocyanate level (ex. equivalent to all cyanurate-biuret formation) produced a clear elastomeric product, DSC break at 225°C, from the 10-mole-percent melamine capped modification. This high melting behavior indicates cyanurate urea and biuret formation. (A similar treatment of the 5-mole-percent modification produced a less satisfactory material, DSC breaks at 125°C, 225°C). Upon storage, however, some bubbles developed in the otherwise transparent elastomer film. This development probably indicates some unreacted isocyanate.

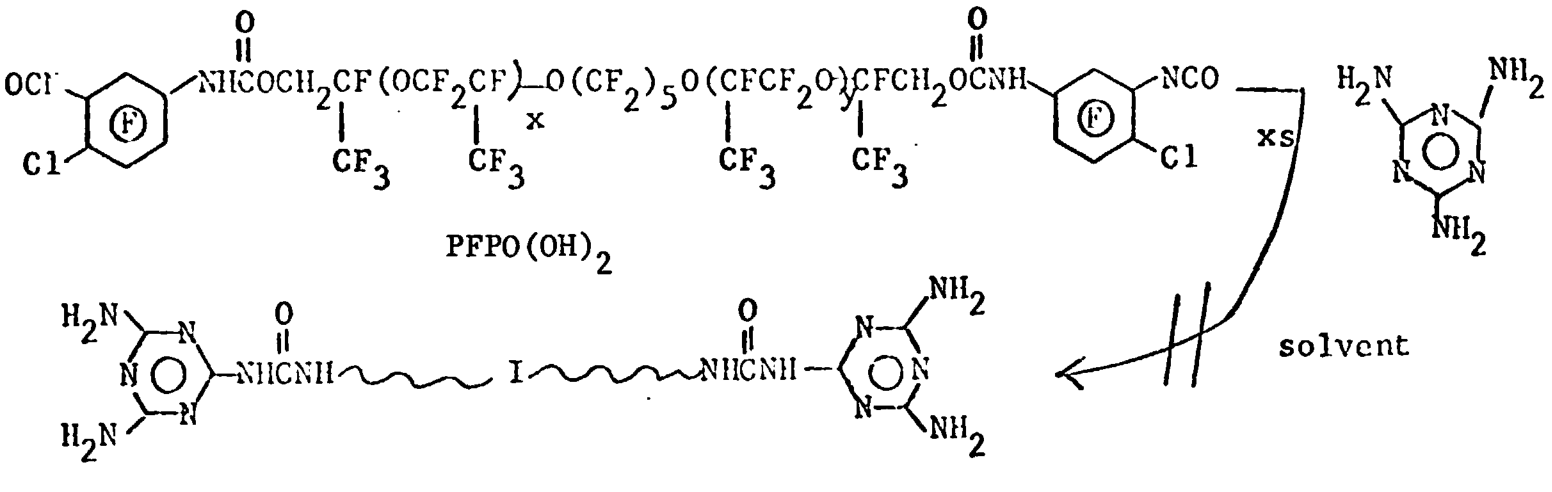
These modifications in curing agent and cure mechanisms all demonstrated profound effects on ultimate polymer properties. In general the more highly-substituted (crosslinked) systems produced considerable upgrading of high-temperature properties. It is felt that even more significant improvements in high temperature characteristics are attainable by judicious choice of candidate curing agents. The LOX-compatibility, oxygen non-flammability criteria impose, however, severe limitations on these materials. An even moderate synthetic effort was beyond the scope of this contract and, as a consequence, the higher temperature capability has yet to be fully demonstrated and evaluated. It is nevertheless quite encouraging that with the modest efforts thus far expended, a significant improvement in these properties has been attained. Further work is definitely indicated and should prove quite fruitful.

IV. CONFORMAL COATINGS

A. Polymer Formulation

Viscosity control and low temperature cure requirements place moderately stringent restrictions on any conformal coating endeavor. Initially we had hoped to prepare some modification of the substituted triazine curing agents which would provide adequate flow characteristics under the conditions of cure. The viscosity of this melamine-terminated prepolymer was shown, however, to be sufficiently high at room temperature to virtually preclude its use in any application where a highly fluid system is needed. An effort was made to take advantage of the improved physical properties imparted by incorporation of melamine as a crosslinking agent while still retaining fluidity in the uncured prepolymer mix system.

A solvented-system approach should be acceptable in conformal coating applications provided: 1) solvent removal can be achieved prior to gellation of the resin system; and, 2) solvent is nonflammable. The reaction of diisocyanate-terminated prepolymer III with melamine in solvent to prepare the "re-capped" IV prepolymer is as follows:



III

This reaction has been previously accomplished in tetrahydrofuran solvent, and subsequently used to prepare transparent elastomers.

It was, therefore, hoped that this prepolymer could be prepared and would be soluble in a solvent which would be nonflammable in a 100% oxygen environment. Three acceptable solvents were investigated for this reaction, with insolubility encountered in all three cases. Melamine was found to be insoluble in all three solvents: hexafluorobenzene, hexafluoro-pentamethylene oxide, and Freon 113. The prepolymer PFPO$(OH)_2$ was found to be soluble in these solvents. Some evidence of reaction was noted by infrared spectroscopy, but unfortunately the "re-capped" (III) prepolymer was also found to be insoluble in these solvents.

Re-capping with melamine was accomplished, as previously, in refluxing tetrahydrofuran. The partially insoluble polymer was isolated with difficulty from excess melamine by centrifugation techniques. The solvent was removed under vacuum and the resulting viscous re-capped prepolymer (IV) was found to be insoluble in the three nonflammable solvents utilized above.

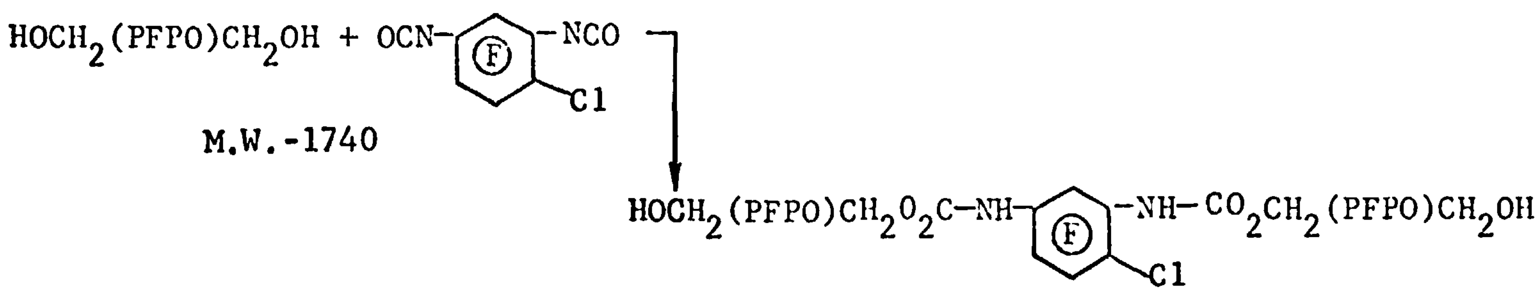
Alternatively we turned our attention to the allophanate-cured UPFPO$(OH)_2$ and PFPO-DI systems. These systems were shown to possess almost ideal characteristics for conformal coating applications. It was initially feared that the high reactivity of the isocyanate moiety would cause excessive bubble (CO_2) formation when thin uncured prepolymer mixes were exposed to atmospheric moisture. This did not prove to be the case, however. Clear, bubble-free coatings were obtained which showed very good substrate bonding characteristics. The effect (if any) of moisture does not interfere with cure. Infrared spectra of cast films which were cured under anhydrous and ambient conditions showed no significant differences. Infrared reflectance measurements (on coated aluminum) using a continuously variable ATR (attenuated total reflectance) unit likewise showed only marginal differences when compared with cast films cured under anhydrous conditions. One would expect a marked difference in the 1600 to 1700 cm^{-1} region if significant amount of hydrolysis (followed by subsequent urea formation) had occurred.

A number of formulations were compounded with the ultimate aim of obtaining continuous, tough films which would perform well in the prescribed application. The screening technique was carried out on aluminum foil, which was meant to simulate the circuit boards. This approach, while effective, nevertheless displayed certain limitations.

The aluminum panels were treated similarly, namely:

1. solvent degrease
2. etch
3. oven dry at 150°F

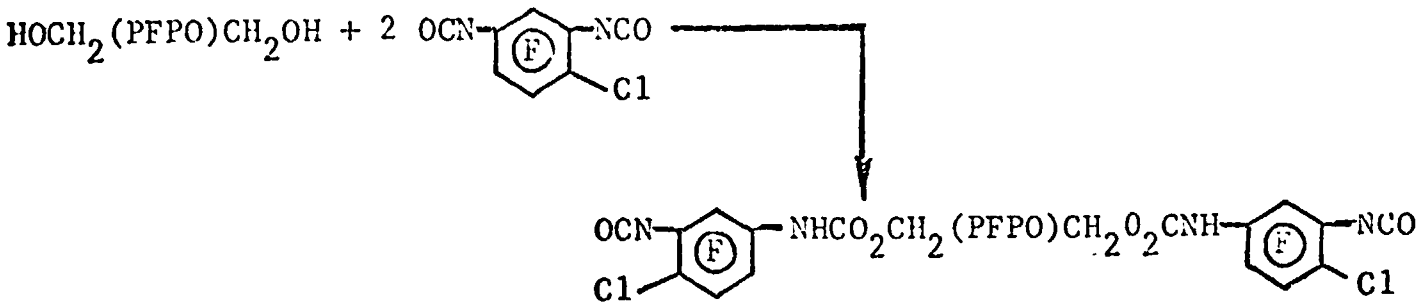
Initial experiments were run using the hydroxyl-terminated urethane extended $UPFPO(OH)_2$ and 1-chloro-3,4,6-trifluoro-m-phenylene diisocyanate. The following flow diagrams show the sequencing and observations during and after specimen preparation and cure.



UPFPO(OH)

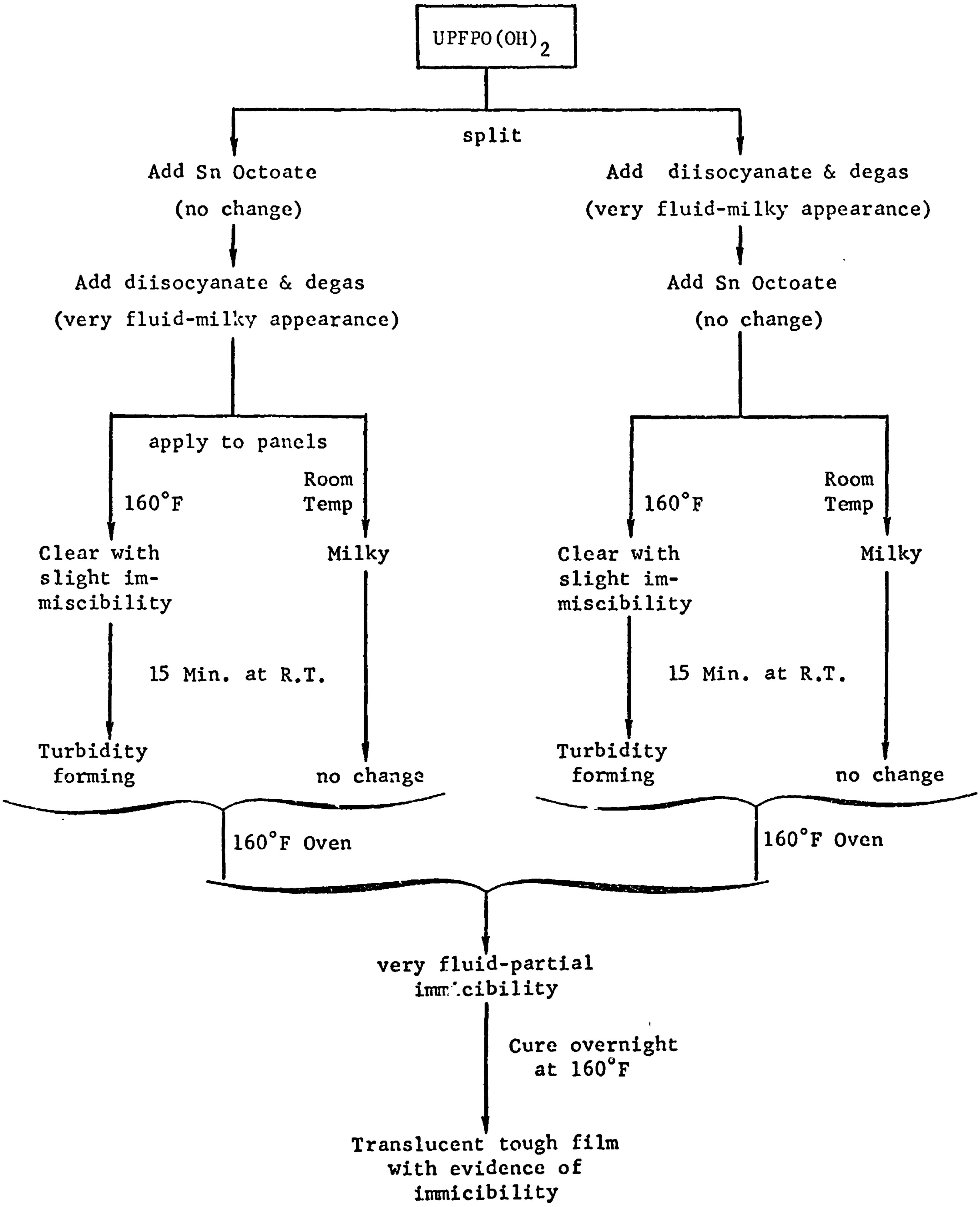
The resulting films showed localized bubbles which may be attributable to local high concentrations of diisocyanate, which in turn reacted with residual surface moisture. In any case, the lack of total solubility was notable and certainly not desirable.

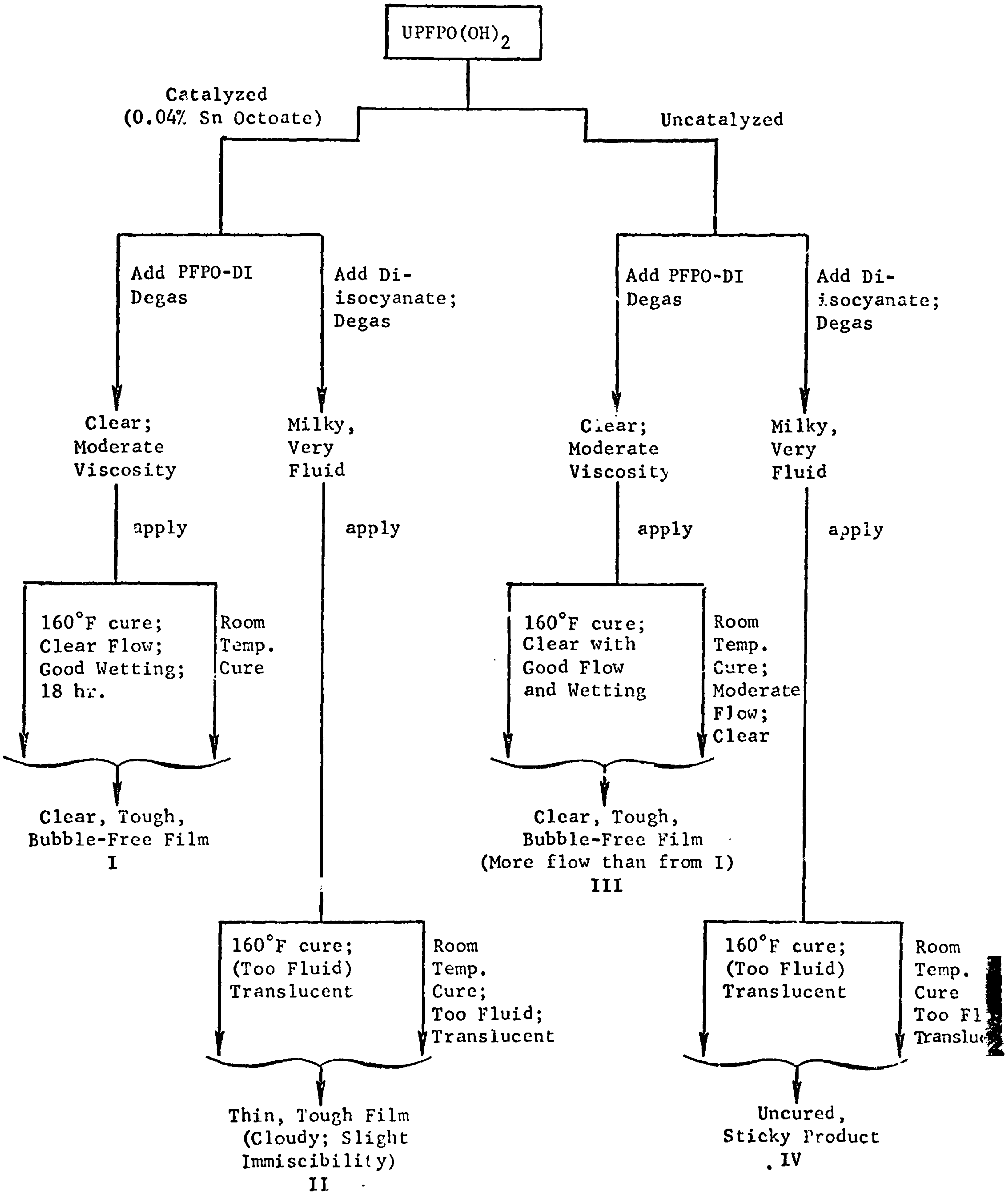
A different series was prepared with some outstanding results. An isocyanate-terminated prepolymer was prepared as follows:



PFPO-DI

This system was completely miscible with the hydroxyl-terminated prepolymer mentioned above. As anticipated, the use of a completely homogeneous polymer premix resulted in films of outstanding clarity and toughness.


UPFPO(OH)$_2$
split
Add Sn Octoate
(no change)
Add diisocyanate & degas
(very fluid-milky appearance)
Add diisocyanate & degas
(very fluid-milky appearance)
Add Sn Octoate
(no change)
apply to panels
160°F
Room Temp
Clear with slight immiscibility
Milky
15 Min. at R.T.
Turbidity forming
no change
160°F
Room Temp
Clear with slight immiscibility
Milky
15 Min. at R.T.
Turbidity forming
no change
160°F Oven
160°F Oven
very fluid-partial immicibility
Cure overnight at 160°F
Translucent tough film with evidence of immicibility


UPFPO(OH)2
Catalyzed (0.04% Sn Octoate)
Uncatalyzed
Add PFPO-DI Degas
Add Di-isocyanate; Degas
Add PFPO-DI Degas
Add Di-isocyanate; Degas
Clear; Moderate Viscosity
Milky, Very Fluid
Clear; Moderate Viscosity
Milky, Very Fluid
apply
apply
apply
apply
160°F cure; Clear Flow; Good Wetting; 18 hr.
Room Temp. Cure
160°F cure; Clear with Good Flow and Wetting
Room Temp. Cure; Moderate Flow; Clear
Clear, Tough, Bubble-Free Film
I
Clear, Tough, Bubble-Free Film (More flow than from I)
III
160°F cure; (Too Fluid) Translucent
Room Temp. Cure; Too Fluid; Translucent
160°F cure; (Too Fluid) Translucent
Room Temp. Cure Too Fl Translu
Thin, Tough Film (Cloudy; Slight Immiscibility)
II
Uncured, Sticky Product
IV

The above coatings were formulated in such a manner that the final overall NCO/OH ratio was the same in all cases (1.8 NCO/1 OH). This is the ratio previously established as optimum for adhesives applications. It has yet to be ascertained whether or not this same ratio is optimum for coating applications. This will be determined in future work.

Since the new forward/reverse-capped combination systems appeared so attractive, two specimen circuit boards provided by NASA-Huntsville were coated (with components mounted) with formulations I and III. The circuit boards were cleaned in isopropanol followed by trichloroethylene and oven-dried at 150°F. The polymer premix was applied by using a stiff bristle brush. Aluminum panels were concurrently prepared and the four specimens were cured in a vertical position in a circulating air oven for 65 hours at 150°F. All four coatings were tough, glossy and tightly bonded to the substrate. These samples were forwarded to the Marshall Space Flight Center for inspection.

Sample discs (2 in. x 1/8 in.) of this same polymer formulation were also submitted to MSFC for dielectric testing. Sample films were also forwarded for flammability and LOX-compatibility testing.

B. Effect of Variation in NCO/OH Ratio

The effects on adhesion (tensile shear) with variations in the overall NCO/OH ratio have already been described above. The bulk resin properties were also investigated. The properties studied were: (1) thermal coefficient of expansion; (2) penetrometer studies (10 g/cm^2 load); and, (3) differential thermal analysis.

Good correlation was found between the penetrometer study and thermal expansion curves. The T_G as determined by DTA was also generally in close agreement, with the exception of one anomalous result, namely with the 1.5/1 NCO/OH system. These values will be rechecked.

TABLE IV

BULK RESIN PROPERTIES AS A FUNCTION OF NCO/OH RATIO

	Thermal Exp. Coefficient (in/in/°C)					
NCO/OH	-80°C	-20°C	+80°C	Penetrometer 10 g/cm^2 load	T_G by DTA	Hardness Shore D
1.8	7.5 x 10^{-5}	1.80 x 10^{-4}	2.62 x 10^{-4}	+18°	22°	56
1.6	9.16 x 10^{-5}	1.71 x 10^{-4}	3.46 x 10^{-4}	+15°	16°	44
1.5	9.63 x 10^{-5}	1.09 x 10^{-4}	2.80 x 10^{-4}	+28°	+1°	42
1.4	8.84 x 10^{-5}	1.24 x 10^{-4}	2.92 x 10^{-4}	0°	-4°	33
1.3	11.8 x 10^{-5}	1.10 x 10^{-4}	-**	-6°	-	55*
1.2	10.3 x 10^{-5}	--	-***	-24°	-	45*

---

* Shore A-2.

** PMT = 60°C

*** PMT = 30°C

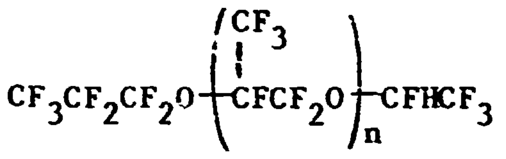
C. Spray Applications

Solvented spray systems have been cursorily examined and results thus far have been most encouraging.

The choice of potential solvent candidates is necessarily limited due to the nonflammability requirement. Any residual solvent would certainly result in a lowering of the physical properties of the cured coating and would likewise impart greater flammability if the solvent itself were flammable.

The solvent system of choice would ideally possess sufficient volatility to allow its facile removal (by evaporation) prior to gellation of the polymer. Too rapid a solvent loss would cause inadequate flow with subsequent imperfect surface characteristics. The optimum solvent system has, as yet, not been developed.

The solubility characteristics of the prepolymer components {UPFPO(OH)$_2$ and PFPO-DI} present an interesting situation. Among those solvents investigated was duPont's E Series Fluids. These nonflammable materials have the following structure:



$$CF_3CF_2CF_2O\left(\overset{CF_3}{\overset{|}{C}}FCF_2O\right)_nCFHCF_3$$

One would anticipate ready solubility of the prepolymer components since by far the majority of the structure consists of perfluoropropyleneoxide. This is not the case, however. Surprisingly, the hydroxy-terminated material is only $\sim$ 10% soluble whereas the isocyanate-terminated material is essentially insoluble.

Other solvents investigated included tetrachloroethylene (which demonstrated very poor solubility characteristics but unaccountably caused very rapid gellation of the polymer mix), hexafluoropentamethylene oxide, Freon 133, and carbon tetrachloride.

Mixed systems of the above mentioned solvents showed no appreciable improvement over a simple solution in Freon 113.

We have successfully sprayed a continuous coating by using the nonflammable Freon-113 as the solvent vehicle. The coatings showed a tendency toward "orange-peeling". This surface effect may be attributed to too rapid a release of rather volatile solvent and to the moderately high viscosity of the resin system inhibiting adequate flow. When the sprayed panels were cured at 160°F the viscosity of the deposited resin was substantially reduced so that only a slight "waviness" was visible in the coatings. They were otherwise highly acceptable. Thus, the cured (160°F for 120 hours) coatings were quite glossy and had a pencil hardness of 4H. Remarkably, the tightly adhered coating successfully passed a 180°

bend over a 1/8 in. mandrel at room temperature and also at -320°F. The scribed coating also successfully passed repeated Scotch-tape adhesion tests.

It is interesting to note that catalyst (stannous octaote) insolubility occurred if the prepolymer components are not mixed prior to dissolution. If premixed, there was no evidence of insolubility.

Ten square feet of 0.003 in. dead soft aluminum foil was coated using a lacquer at 20% solids level and was submitted to MSFC for test and evaluation.

CONCLUSIONS

The results of the work accomplished to date may be summarized as follows:

I. Adhesive Formulation

A. Allophanate Cured System

Lap shear strengths have been significantly upgraded in the cryogenic and moderate (< 150°F) temperature regions. Values of 6000 to 7500 psi are consistently obtainable at liquid nitrogen (-320°F) temperatures. Room-temperature strengths have been improved to such an extent to permit expectations of reproducible bond strengths in the range of 2300 to 2500 psi. Major improvements in ease of handling and storage stability have likewise been strongly demonstrated.

B. Improved High-Temperature Performance

The feasibility of marked improvement in upper temperature properties has been amply demonstrated by the incorporation of cyanoguanidine and amine-terminated PFPO as curing agents. The nonflammability criterion imposes a severe limitation on prospective amine-type curing agents, but it is felt that suitable materials are amenable to synthesis. Such an approach is certainly warranted based on the evidence already in hand.

II. Conformal Coatings

Concurrent with the overall improvements in adhesive formulation brought about by utilization of the two-prepolymer UPFPO$(OH)_2$ and PFPO-DI system, the area of conformal coatings and embedment compounds has been brought much closer to full fruition. Diversified application techniques, including dip-, spray-(solvented) and brush- have been investigated and shown to be readily suitable. High gloss, tough, continuous coatings have been routinely prepared using all these techniques. The optimum formulation has not yet been finalized.

III. Analysis and Preparation of PFPO$(OH)_2$

Vapor-phase chromatography has been shown to be an effective tool for thorough analysis and molecular weight determination of hydroxyl-terminated PFPO$(OH)_2$. Rapid, accurarate analyses are the result of the work described in the body of this report. The achievement of this goal allows an optimization program to proceed under much more closely controlled conditions which should finally result in obtaining polymer with the most desirable characteristics.

RECOMMENDATIONS FOR FUTURE WORK

The major follow-on efforts should be in those areas already treated at length above in the body of the report. It is felt that emphasis on derived systems to impart improved thermal capability should result in corollary improvements in adhesion and polymer toughness. Certainly these efforts should include significant work directed toward synthesizing potential urea-forming (amine/isocyanate) moieties in addition to those others already mentioned (melamine, etc.).

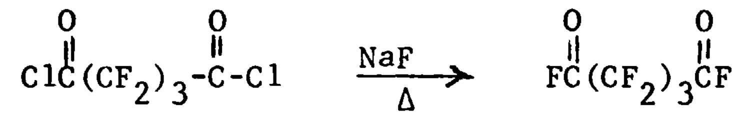
New- and modified-curing agents should be structured to provide a minimum (or no) flammability sensitivity. Consequently, the highest promise of success will lie in those materials which possess no (or a minimum) of carbon-hydrogen bonds. Hence the efforts should be directed toward development of perfluorinated aromatic di- and tri-amines and suitably substituted heterocyclic systems.

Improvements in solvented coating application may be expected following an extensive study of applicable solvent systems. A less volatile non-flammable system is needed before high perfection coatings can be prepared on an easily processable reproducible basis.

EXPERIMENTAL

TYPICAL PREPARATION OF HYDROXYL-TERMINATED POLYPERFLUOROPROPYLENE OXIDE [PFPO(OH)$_2$]

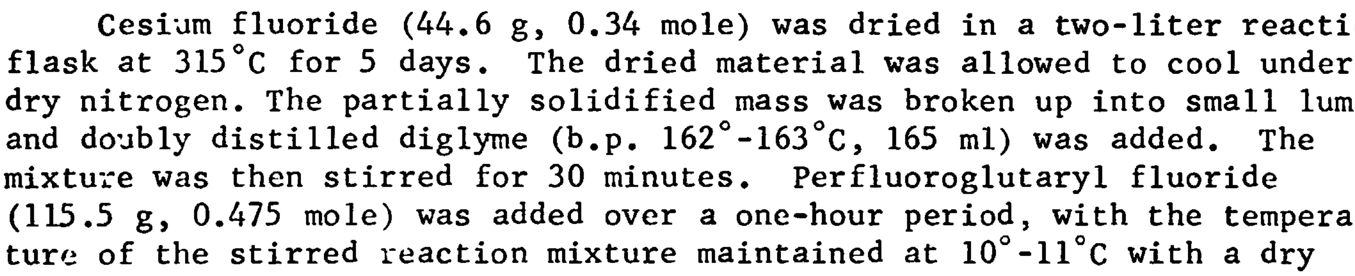
A. Preparation of Perfluoroglutaryl Fluoride



$$\mathrm{Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl} \xrightarrow[\Delta]{NaF} \mathrm{F\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}F}$$

Sodium fluoride (731 g, 17.5 mole) was dried overnight 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 (2100 ml) was added and stirring begun. Perfluoroglutaryl chloride (1328 g, 4.75 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 (49°C) for 5 hours. After standing (under nitrogen) overnight, the volatile material (< 49°C b.p., 746 g) was isolated by distillation and then 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 730 g.

B. Polymerization of Perfluoropropylene Oxide



$$\mathrm{CF_3\text{-}CF\text{-}CF_2}\ (\text{epoxide, O bridging } \mathrm{CF}\text{-}\mathrm{CF_2}) + \mathrm{F\text{-}\overset{O}{\overset{\|}{C}}(CF_2)_3\text{-}\overset{O}{\overset{\|}{C}}F} \xrightarrow{CsF} \mathrm{F\overset{O}{\overset{\|}{C}}\text{-}\overset{CF_3}{\overset{|}{C}}F\ (OCF_2\overset{CF_3}{\overset{|}{C}}F)O(CF_2)_5O(\overset{CF_3}{\overset{|}{C}}FCF_2O\text{-}\overset{CF_3}{\overset{|}{C}}F\text{-}C{\overset{O}{/\!\!/}}F}$$

$$+$$

$$\mathrm{CF_3CF_2CF_2O(\overset{CF_3}{\overset{|}{C}}FCF_2O)\overset{CF_3}{\overset{|}{C}}F\text{—}\overset{O}{\overset{\|}{C}}F}$$

Cesium fluoride (44.6 g, 0.34 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, 165 ml) was added. The mixture was then stirred for 30 minutes. Perfluoroglutaryl fluoride (115.5 g, 0.475 mole) was added over a one-hour 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 (25.0 g, 0.15 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 (975 g, 5.85 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 965 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	27-42	0.3-0.1	125.4 g
Cut II	24-40	0.05-0.07	129.3 g
Cut III	43-61	0.10-0.06	26.1 g
Cut IV	64-96	0.10-0.07	44.1 g
Cut V	93-126	0.06-0.08	410.3 g
Cut VI	135-148	0.08-0.10	73.3 g
			808.5 g collected

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

The molecular weight of Cut V 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:

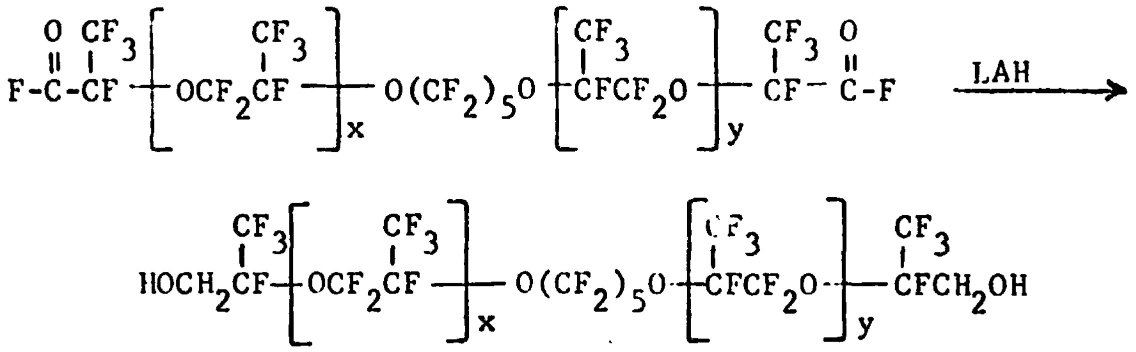
> Place 75.00 ml of standardized 0.1N NaOH in a 250 ml flask. Add 10 ml of 5% pyridine in water solution. Weigh in 3 to 4 milliequivalents of PFPO acid fluoride. Stopper the flask and shake for at least 2 hours and until clear. Titrate with standardized 0.1N hydrochloric acid to the phenol-phthalein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

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

Sample Results

Sample	Equivalent Weight (as above)	Molecular Weight by VPO in Freon 113	Indicated Functionality
Cut V	679, 681, 682	1356, 1366	2.00

C. Reduction of Acyl Fluoride-Terminated Polyperfluoropropylene Oxide



$$F\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{CF_3}{\overset{|}{CF}}\left[OCF_2\overset{CF_3}{\overset{|}{CF}}\right]_x O(CF_2)_5O\left[\overset{CF_3}{\overset{|}{C}}FCF_2O\right]_y\overset{CF_3}{\overset{|}{CF}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}F \xrightarrow{LAH}$$

$$HOCH_2\overset{CF_3}{\overset{|}{CF}}\left[OCF_2\overset{CF_3}{\overset{|}{CF}}\right]_x O(CF_2)_5O\left[\overset{CF_3}{\overset{|}{C}}FCF_2O\right]_y\overset{CF_3}{\overset{|}{CF}}CH_2OH$$

PFPO(OH)$_2$

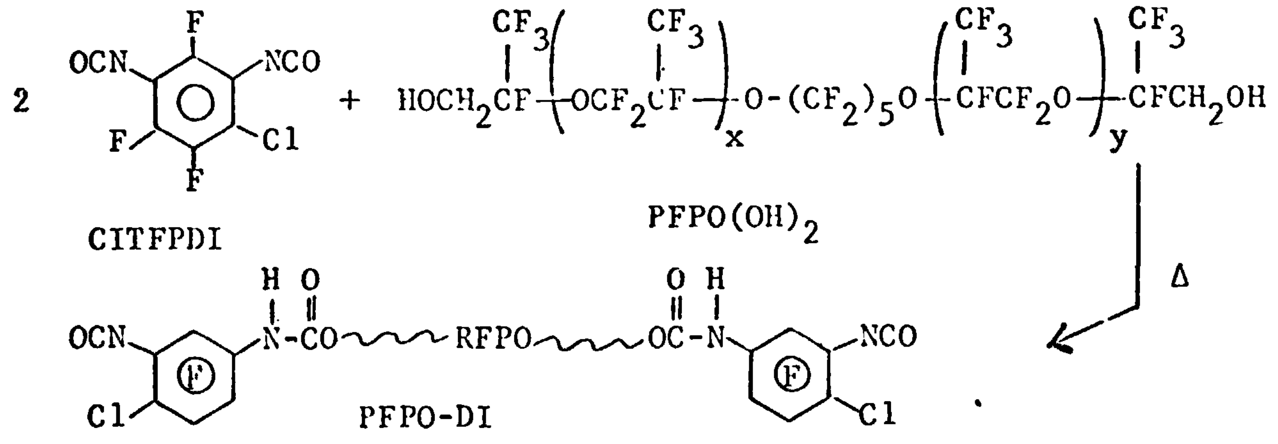
Lithium aluminum hydride (112.5 g, 2.96 mole) was carefully added to dry tetrahydrofuran (5400 ml) in a 12 liter Morton flask and stirred for one hour. Crude unfractionated polyperfluoropropylene oxide (1590 g) was added over a four-hour period using external cooling to maintain the temperature between 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, yielding 1494 g of crude product. Vacuum fractionation resulted in the following fractions:

Fraction	Boiling Range	mm Hg	Total Weight
1	26-70°	0.4-0.5	103.3 g
2	65-67	0.3-0.4	147.4
3	68-82	0.3-0.4	136.2
4	83-173	0.2-0.3	944.2
			1331.1 g collected

In addition, 163 g of low boiling material was caught in the dry ice/acetone traps.

Fraction No. 4 had a molecular weight of 1740 by VPO determination in THF. The data plot showed a marked negative curvature with a non-zero extrapolated (zero concentration) intersection.

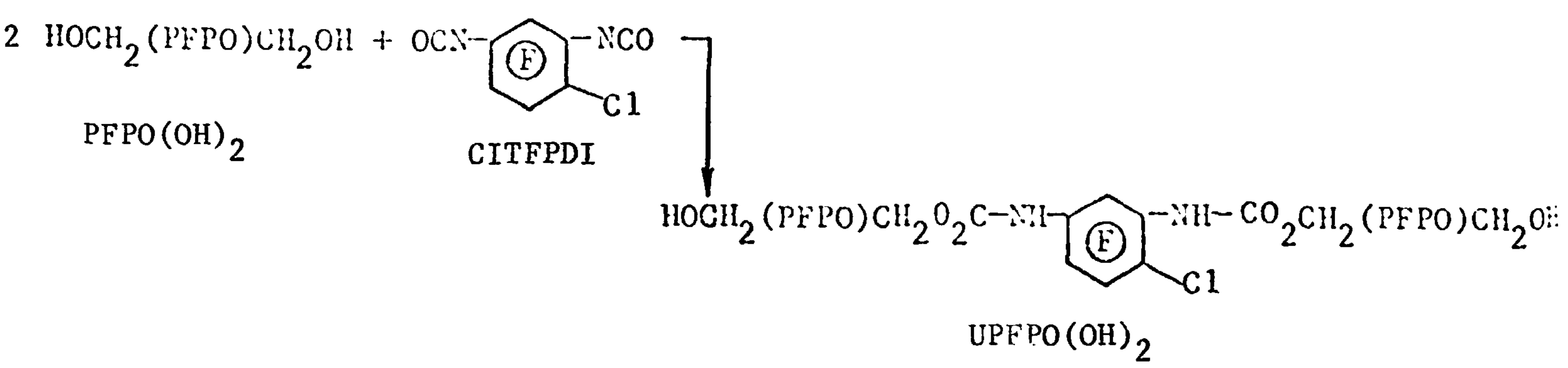
PREPARATION OF ISOCYANATE-TERMINATED POLYPERFLUOROPROPYLENE OXIDE PREPOLYMER (PFPO-DI)



Hydroxyl-terminated polyperfluoropropylene oxide $PFPO(OH)_2$ (30.8 g, 0.0200 mole) was charged to a resin kettle under dry nitrogen and 6-chloro-2,4,5-trifluoro-m-phenylene diisocyanate (10.5 g, 0.0423 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

86°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 2 hours at a temperature of 90°-95°C, the system was thoroughly evacuated (at ~ 95°) and excess diisocyanate removed with vacuum.

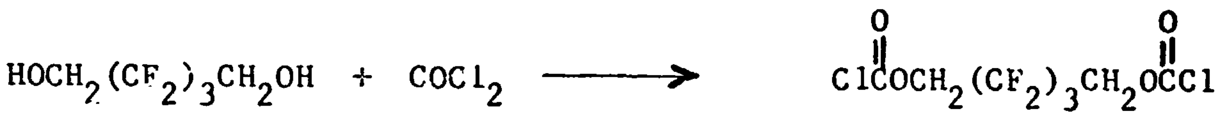
PREPARATION OF URETHANE-EXTENDED HYDROXYL-TERMINATED POLYPERFLUOROPROPYLENE OXIDE-UPFPO(OH)$_2$



A mixture of PFPO(OH)$_2$ (30.8 g, 0.020 mole) and ClTFPDI (2.63 g, 0.0105 mole) was stirred overnight at 90°-100°C under a dry N_2 atmosphere. The cloudy, easily-pourable liquid was divided into two equal portions. Stannous octoate (6.7 mg, 0.04% by weight) was added to one-half. There was no apparent difference between the catalyzed and the uncatalyzed half after prolonged (> 6 months) storage at room temperature. Shear strengths of adhesive prepared from recently catalyzed and the stored catalyzed material were essentially equivalent.

PREPARATION OF HYDROXYL-TERMINATED POLYHEXAFLUOROPENTAMETHYLENE CARBONATE

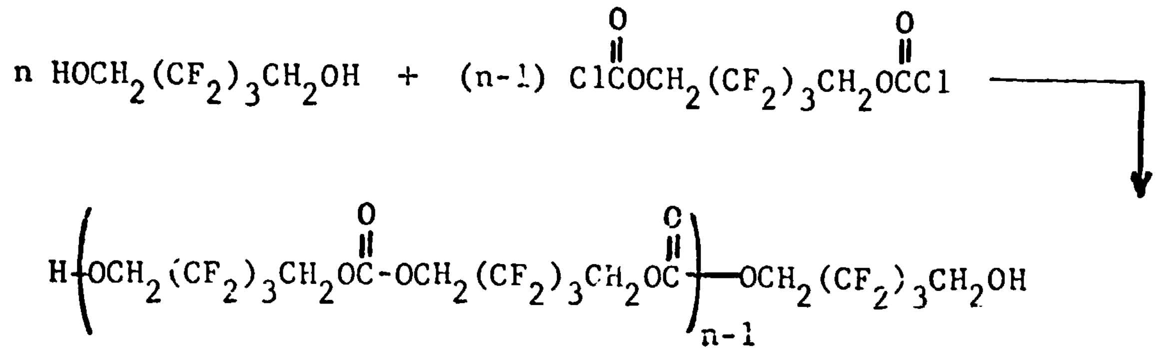
A. Preparation of Hexafluoropentamethylene-Bischloroformate



$$HOCH_2(CF_2)_3CH_2OH + COCl_2 \longrightarrow Cl\overset{O}{\overset{\|}{C}}OCH_2(CF_2)_3CH_2O\overset{O}{\overset{\|}{C}}Cl$$

Phosgene (450 g, 4.6 mole) was condensed into diethyl ether (8 liters) at -10-0°C. Pyridine (332 g, 4.2 mole) was then added over a period of 30 minutes with rapid stirring, producing a slurry of chlorocarbonylpyridinium chloride.Hexafluoropentanediol (424 g, 2.0 mole) in diethyl ether (1000 ml) was added over a 2-hour period and the temperature allowed to come to ambient. Stirring was continued for 4 hours. The reaction mixture was then filtered under dry nitrogen and allowed to stand overnight. The solvent was then removed from the clear solution under reduced pressure (40°C). Vacuum fractionation of the remaining mobile liquid was carried out. The fraction boiling between 82°-86°C at 2-4 mm was collected. Vapor phase chromatography indicate purity > 99.7%. Total yield was 326 g (48%).

B. Preparation of Hydroxyl-Terminated Polyhexafluoropentamethylene Carbonate



$$n\ HOCH_2(CF_2)_3CH_2OH + (n-1)\ Cl\overset{\overset{O}{\|}}{C}OCH_2(CF_2)_3CH_2O\overset{\overset{O}{\|}}{C}Cl \longrightarrow H\left(OCH_2(CF_2)_3CH_2O\overset{\overset{O}{\|}}{C}-OCH_2(CF_2)_3CH_2O\overset{\overset{O}{\|}}{C}\right)_{n-1}OCH_2(CF_2)_3CH_2OH$$

Hexafluoropentanediol (84.8 g, 0.40 mole) was dissolved in dry tetrahydrofuran (150 ml). Pyridine (32.4 g, 0.41 mole) was added and the mixture cooled to ~ 5°C. Hexafluoropentamethylene-bischloroformate (67.4 g, 0.20 mole) in THF (50 ml) was added with stirring over a one-hour period. The temperature was kept at < 15°C during the addition, then stirred overnight at room temperature. The slightly pink precipitate of pyridinium chloride was filtered off and the resulting water-white solution was poured into one liter of water, which had been acidified with 20 ml of conc. HCl, and vigorously stirred. After settling, the aqueous layer was removed by decantations and the acid wash was repeated. The viscous oil was then washed twice with distilled water (2 x 1000 ml). After the final water wash, the white viscous oil was taken up in THF and dried over $MgSO_4$ overnight. Following filtration and vacuum removal of solvent (at 90°C) a pale yellow very viscous oil was obtained which slowly solidified over a period of several days; yield 109.1 g (79.5%).

Vapor pressure osmometry showed the following results:

Molecular Weight Theory	Molecular Weight Found
688	715

PREPARATION OF THE POLYURETHANE (NCO/OH = 1.8/1)

PFPO-DI (21.10 g, 0.009 mole) and the hydroxyl-terminated polycarbonate (3.57 g, 0.005 mole) were charged to a resin kettle at ~ 60°C and 5 drops of uversol iron liquid (6% Fe) catalyst were added and the mixture stirred 10 minutes. After vacuum degassing, tensile shear bonds were prepared as above and cured overnight at 175°F.

A bubble-free film was prepared similar to that above.

The calculation for the overall NCO/OH ratio is described below. More meaningful results are obtainable if the overall NCO/OH value is used rather than simply the ratio of the curing terminations in the dual prepolymer UPFPO$(OH)_2$ and PFPO-DI.

The prepolymers may be schematically diagrammed as follows:

$$A = \text{ClTFPDI}$$
$$B = \text{PFPO(OH)}_2$$

then $\text{UPFPO(OH)}_2 = \text{BAB} = (1A, 2B)$

$\text{PFPO-DI} = \text{ABA} = (2A, 1B)$

if we let $\alpha = \text{PFPO-DI}$

$\beta = \text{UPFPO(OH)}_2$

We obtain the following vector equations where the NCO/OH ratio is 1.8/1 as an example

$$\alpha(2,1) + \beta(1,2) = (1.8, 1)$$

Scalar multiplication yields the following equations

$$2\alpha + \beta = 1.8$$

$$\alpha + 2\beta = 1$$

Solving for α and substituting we get

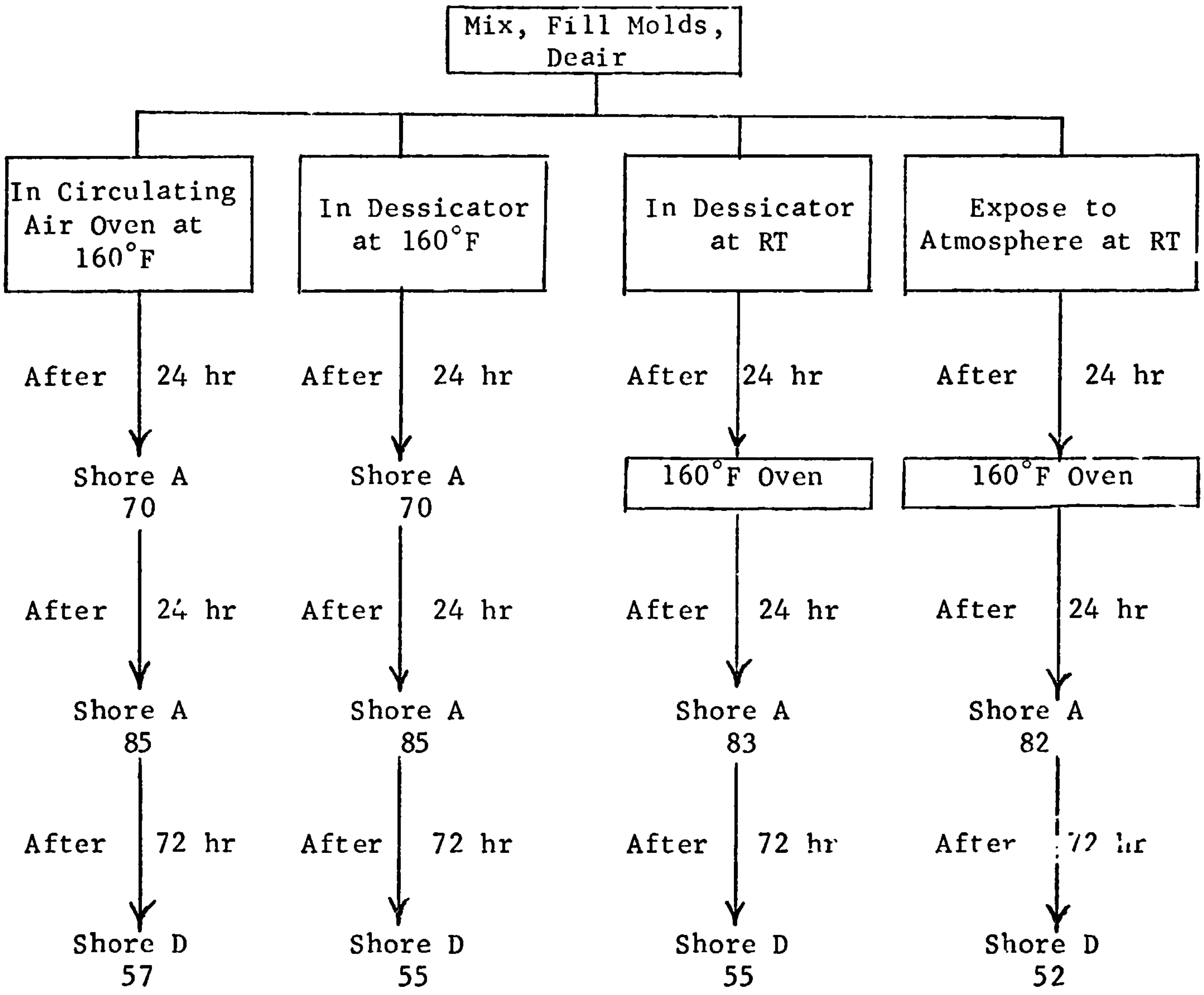
$$\alpha/\beta = 13/1$$

as the mole ratio of PFPO-DI/UPFPO$(OH)_2$ for an overall NCO/OH ratio of 1.8/1.

EFFECT OF CURE CYCLE PARAMETERS ON HARDNESS PROPERTIES OF PFPO-DI/UPFPO$(OH)_2$ SYSTEM

The following experiment was run to establish the cure cycle necessary for fully-cured resin and to establish the effect of moisture on the cured polymer.

PFPO-DI (4.43 g, 0.00217 mole) and UPFPO$(OH)_2$ (0.55 g, 0.000167 mole containing 0.04% Sn octoate) were mixed in a small bearker, degassed and poured into four small cavity molds. After further degassing, the four samples were treated as follows:



The cured material show no bubbles and there was no discernable difference in the four specimens.