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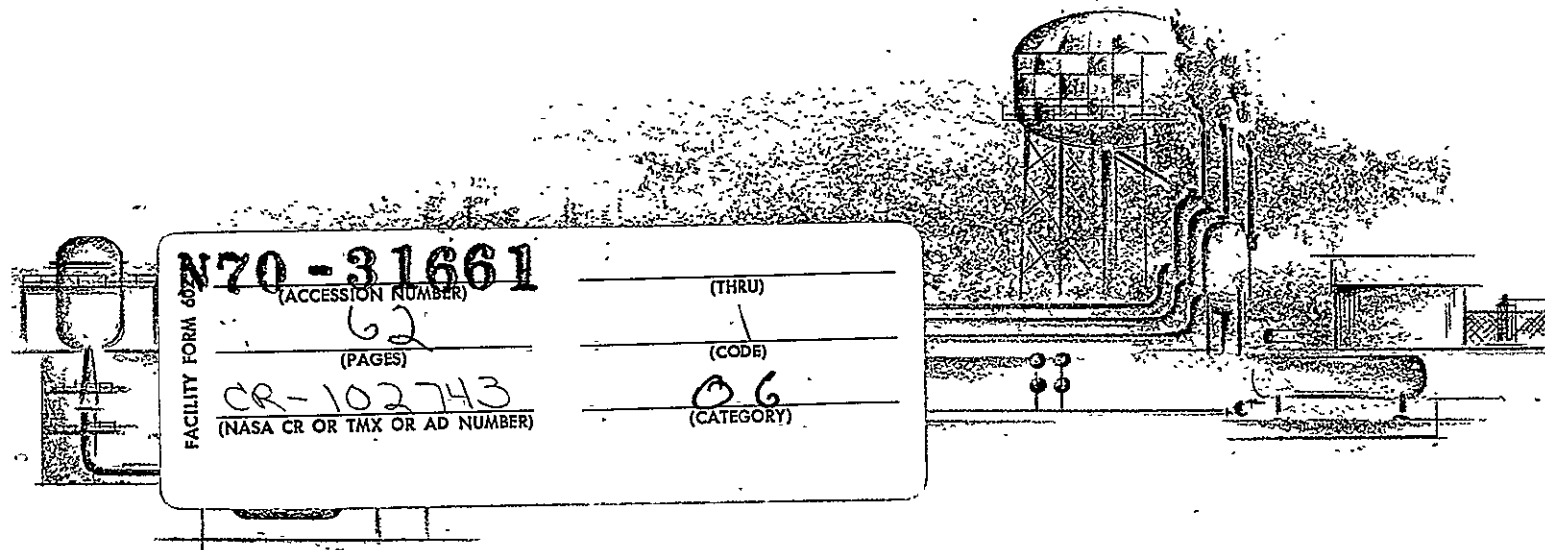
DEVELOPMENT OF CONFORMAL COATING MATERIAL

Samuel A. Glickman
Gerard G. Sonenstein

Report Period: June 1, 1969 - December 31, 1969

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Thiokol CHEMICAL CORPORATION O REACTION MOTORS DIVISION

DEVELOPMENT OF CONFORMAL COATING MATERIAL

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Gerard G. Sonenstein

Report Period: June 1, 1969 - December 31, 1969

Report RMD 5188-F
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FOREWORD

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ABSTRACT

Conformal coatings for electronic circuit boards and free films were obtained from a formulated solvent-based solution of gum CNR (tetrafluoroethylene, trifluoronitrosomethane, nitrosoperfluorobutyric acid gum terpolymer) reinforced with silica and cured with a diepoxide. These coatings displayed transparency, nonflammability, high strength, excellent vibration protection character among other satisfactory properties. A large batch was prepared for NASA's subsequent use.

Liquid carboxylic nitrosofluorocarbon polymers have been obtained from trifluoronitrosomethane, tetrafluoroethylene, nitrosoperfluorobutyric acid terpolymerization modified by the joint use of chlorine and Freon 113 solvency. Diepoxide cured coatings have been obtained with good promise for use in conformal coatings.

Unsaturated terpolymers and carboxylic unsaturated tetrapolymers were prepared and oxidized to give liquid carboxylic nitrosofluorocarbon polymers. Cured films have been obtained therefrom.

Hydroxyl functioned nitrosofluorocarbon polymers have been obtained by the reaction of ethylene oxide and a liquid carboxylic polymer. Cure with a fluorinated arylene diisocyanate has been examined.

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I. SUMMARY

The objective of this program is the development of a polymeric conformal coating for electronic circuitry. The requisite properties are transparency, flexibility, low modulus of rigidity, vibration protection among other essential characteristics. A workable viscosity, adequate application life, good adhesion and nonflammability stand as additional requisite aims of conformal coating candidates.

The program was approached from two concurrent directions: (a) preparation of a gum-solvent coating composition using high molecular weight carboxynitrosorubber (CNR) and a diepoxide curative, and (b) the preparation of a solventless, liquid prepolymer of the class of nitrosofluorocarbons containing an active hydrogen cure site of the nature of carboxyl or hydroxyl.

A CNR-gum solvent composition, eminently suitable for conformal coating application, has been formulated with a requisite diepoxide curative. This formulation has been successfully applied to electronic component-equipped circuit boards and has been shown to meet many of the specified requirements. Cured films have been prepared which satisfy a number of the requisite properties.

Liquid carboxylic nitrosofluorocarbon polymers (liquid CNR) have been obtained by the combined use of chlorine and Freon 113 solvent in a modified terpolymerization reaction. Requisite viscosities and functionalities have been achieved. Diepoxide cure by means of dicyclopentadiene diepoxide gave coatings of excellent transparency, flexibility, adhesion and complete cure characteristics.

Ozonolysis of unsaturated terpolymer has been performed by means of ozone at atmospheric pressure. The preparation and ozonolysis of unsaturated carboxylic nitrosofluorocarbon polymer has been achieved. Cure reactions of these terminal dicarboxylic acids and polycarboxylic acids have been examined.

The reaction of ethylene oxide and liquid CNR has been studied. The near-effective utilization of all the carboxyl groups requires close to four moles of ethylene oxide. The hydroxyl containing polymer has been cured with a fluorinated diisocyanate.

II. INTRODUCTION

A highly reliable conformal coating is required by NASA/MSFC for the protection of electronic circuitry in spacecraft. This coating material must primarily be transparent, flexible through a wide temperature range (-65 to 100°C), nonflammable (in oxygen-enriched atmospheres) and exert a minimum stress on components and solder joints when cured or thermally cycled between -65 and 100°C. The candidate system must also resist vibration loading to 100 G and conform to the detailed requirements cited in the contract and MSFC Spec. 393A.

Nitrosofluorocarbon polymers having active cure sites appeared signally of value for investigation for this application because preliminary screening and an earlier program had indicated that these polymers satisfy many of the properties desired.

The scope of the present program was directed towards:

- Synthesis of liquid nitrosofluorocarbon polymers having carboxyl, hydroxyl and amide functions.

- The investigation of cure reactions with diepoxides and diisocyanates of the above polymers.

- Development of solvent-coating systems based on CNR elastomer gum.

- Preliminary evaluation of the most promising coatings for application and working properties.

- Screening for critical properties.

- Detailed evaluation and testing of film properties obtained for a selected candidate composition.

III. TECHNICAL DISCUSSION

The development of a transparent conformal coating was approached from two concurrent directions: (a) the preparation of a gum-solvent coating composition using high molecular weight carboxynitrosorubber (CNR) and a diepoxide curative, and (b) the preparation of a solventless, liquid prepolymer of the class of nitrosofluorocarbons containing an active hydrogen cure site of the nature of carboxyl or hydroxyl.

A. CNR-Gum Solvent Coating System

1. Formulation

a. Gum Polymer - The carboxy nitrosorubber gum polymer (CNR of Thiokol Chemical Corp.) used in this investigation is a high molecular weight terpolymer of tetrafluoroethylene, nitrosotrifluoromethane and nitrosoperfluorobutyric acid. The material is identified as:

> Batch No. A-021 (Thiokol Chemical Corp.)
> M.W. (intrinsic - viscosity method) ~570,000
> Acid content (mole %)   0.57

b. Solvents - Various solvent systems for brushing were evaluated and the following blend seemed to provide the best balance between solvent efficiency in obtaining stable, high solids solutions, fast drying at ambient temperatures and total release of volatiles after a short postcure (@ 80 °C):

Solvent Type	B.P.	Wt. %
FC-77 (fluoroether - 3M Co.)	207°F	40.0
1,3-Di-(trifluoromethyl) benzene	239°F	30.0
Halocarbon-112A (chlorofluorocarbon)	198°F	20.0
Freon-113 (chlorofluorocarbon)	117.6°F	10.0

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Gum solutions containing 15.0 wt. % CNR solids were prepared by adding strips of the gum to the agitated solvent mixture follcwed by stirring for several hours at ambient temperature. Heating at 45-50°C lessened the time for homogenization of the mixture.

c. <u>Curatives</u> - Chromium trifluoroacetate, used traditionally as a curative for CNR gum in many applications, was eliminated from further consideration for a number of reasons. They are: opacity of film, use of cure temperatures of 200°C or higher, shrinkage and poor electrical properties associated with release of trifluoroacetic acid at insufficient cure temperatures of the present application (82°C).

Cycloaliphatic diepoxides had been examined in earlier Thiokol Chemical Corporation research as curatives for CNR. The compound which appeared to be ideally suited for use in a CNR conformal coating was ERLC-4207, a mixture of 75.5% exo/24.5% endo dicyclopentadiene diepoxide (Union Carbide Corp.). It is normally a liquid or can be readily liquefied by warming at about 130°F for a short time.
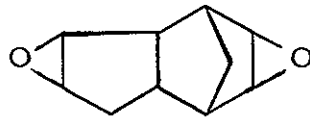
ERLC-4207 (Union Carbide Corp.)

The chemical reaction ensuing between the cure site and the curative may be depicted:

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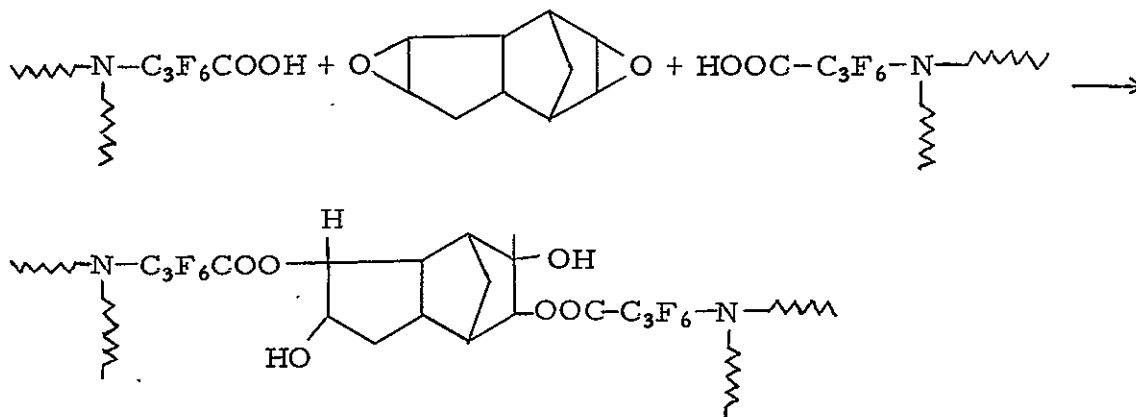
A degree of crosslinking may occur via an esterification or reaction of diepoxide with the newly formed hydroxyl groups.

A brief study was made to establish the optimum curative level of ERLC-4207 to obtain the best balance of application properties, working properties vs. cure cycle, overall quality and film strength.

Fig. 1 presents a profile of stress/strain (mechanical) properties as a function of curative level in <u>unreinforced</u> CNR films, applied by brushing 15.0% gum solutions on (silicone) release-coated glass plates. The films were force dried with a blower at room temperature for about 10 to 15 minutes and then tempered in an oven at 80°C for 15 to 30 minutes per coat to ultimate thicknesses of 4.5 to 6.0 mils. As the curves (in Fig. 1) indicate, the best stress/strain value (without reinforcing fillers) seemed to be at the calculated stoichiometric level or ~4.0 pphr/CNR solids and this averaged about 240 psi, tensile strength and 570% elongation as compared with 500-600 psi and 600% specified to be the requirement.

d.   Reinforcement - A number of reinforcing fillers for CNR gum have been investigated with both the CTA and epoxide curing systems; the most effective reinforcements known to date are the colloidal (high surface) silicas, e.g., Hi-Sil 233. In view of the gap between tensile requirements and the best values that were obtained with unreinforced CNR gum solutions (Fig. 1), a subsequent study was made to find a level of Hi-Sil 233 appropriate for upgrading film strength (and elasticity) without sacrificing transparency or quality. The Hi-Sil reinforcement was milled into the gum at levels of 1.0 to 15.0 pphr/CNR. After the coating solutions were prepared containing from 1.0 to 15.0 parts of Hi-Sil, the same level of ERLC-4207 curative (4.0 pphr/CNR gum) was added to each of the samples, applied thickness per coat varying with the silica content. At a Hi-Sil loading of 1 pphr/CNR gum, 9 coats were required to develop a film thickness of 3.0-5.0 mils, at 5 pphr, 8 coats yielded 5.0-6.5 mils, 10 pphr gave 8.0-9.0 mils with 7 coats and 15.0 pphr 7.0-9.0 mils with 4 coats. Considerable thixotropy was apparent in the range of 10-15 pphr that resulted in air entrapment or bubbles in the cured films which would presumably affect quality and strength.

Reference to Fig. 2 indicates that the sample reinforced with 10.0 pphr of Hi-Sil had the best balance between transparency, strength and quality (bubble distribution). This sample was only slightly less transparent than the lower silica levels but considerably better than the 15 pphr level and small print was easily legible through thicknesses of 0.009". It was however much stronger than the unreinforced films (630 psi tensile @ 775% elongation) and far superior in tensile properties to the reinforced samples of lower silica content (see Fig. 2).

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FIGURE 1

MECHANICAL PROPERTIES OF UNREINFORCED
CNR FILMS, VARYING LEVEL OF
EPOXIDE CURATIVE

ALL FILMS RANGED FROM 4.5 - 6.0 MILS THICKNESS
CURE: EACH COAT FORCE-DRIED @ RMT & TEMPERED @ 80°C
X 15 - 30 MIN.

TENSILE STR. (psi) & ELONGATION (%)

700
600
500
400
300
200
100

2.5 PPHR/CNR GUM WAS EVALUATED BUT VALUES NOT REPORTED. FILMS HAD EXCESSIVE BUBBLE DISTRIBUTION & DATA WAS SCATTERED

LEVEL

APPROX. STOICHIOMETRIC

MECHAN. PROPERTIES
TENSILE STRENGTH (psi) =
ELONGATION (%) =

NOTE: *CURATIVE WAS ERLC-4207 (PROPRIETARY)
BLEND OF CYCLOALIPHATIC DIEPOXIDES
SUPPLIED BY UNION CARBIDE.)

0   1.0   2.0   3.0   4.0   5.0

LEVEL OF ERLC-4207 (EPOXIDE) CURATIVE
(PPHR/CNR GUM SOLIDS)

FIGURE 7

EFFECT OF SILICA-LOADING ON STRENGTH & QUALITY
OF EPOXIDE-CURED CNR FILMS
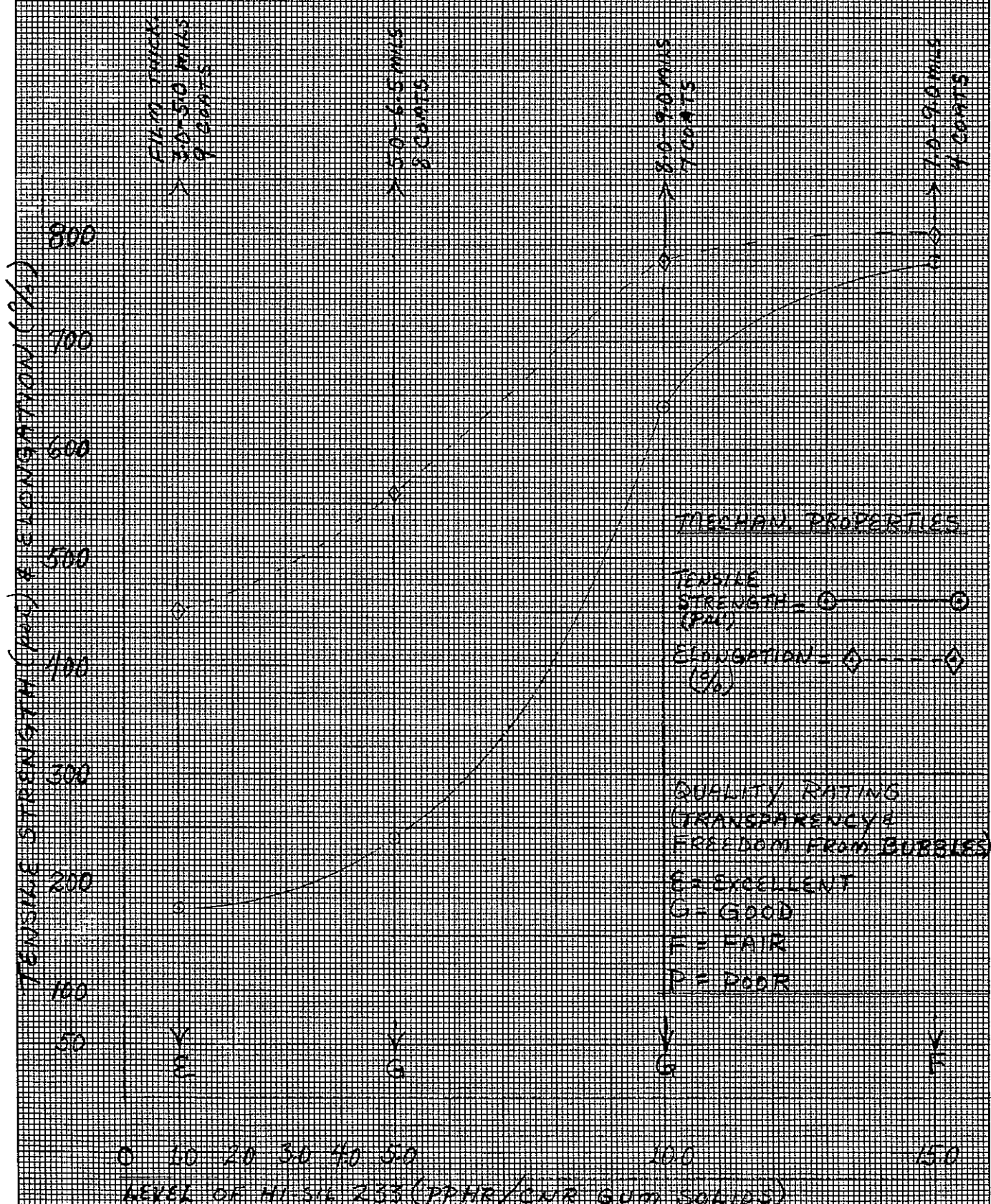
NOTES: CURATIVE WAS ERLC-4207 @ 4.0 PPHR/CNR SOLIDS IN ALL CASES
CURE = EACH COAT FORCE-DRIED @ RmT & TEMPERED @ 80°C X 15-30 min.

e. Surface Active Agents - Another study was undertaken to upgrade film quality by controlling the formation and distribution of bubbles and improving levelling properties and wetting through the reduction of surface tension. The inevitable consequence of dispersing reinforcing silicas in the CNR polymer is a definite increase in yield point due in part to their high specific surface area and also to secondary valence or hydrogen-bonding effects. This engenders some bubble retention during agitation (in making solutions) which may lead to pinholes (or other stress-raisers) in the cured films.

Several types of surface active agents were screened for compatibility and effectiveness in the CNR coating system described. The most effective of these was "Zonyl" A, a proprietary, nonionic alkyl phosphate (supplied by the du Pont Company) that remains chemically stable in the presence of acids, bases, salts, oxidizers and reducing agents.

A final study was conducted to establish the optimum level of Zonyl additive for:

- Suppressing thixotropy at 10 pphr Hi-Sil loading.

- Maintaining low surface tension to prevent bubble formation.

- Enhancing self levelling during coating application.

- Wetting the substrate to promote film adhesion.

Fig. 3 shows graphically the relationship between additive level and stress/strain properties. The optimum level of Zonyl A seems to be 0.05% of total formula weight. At this concentration an average tensile strength of 840 psi and 800% elongation were obtained as compared to 630 psi @ 775% elongation with the same system containing no surfactant (Fig. 2). This sample film had excellent clarity, transparency and was visually bubble free and uniform throughout (no brush marks). At this level of Zonyl (0.05% of formula weight) solution viscosity was 260 cps/#5 spindle/@ 60 rpm and 23°C, well below the maximum of 25,000 cps allowed.

f. Composition and Properties

The final formulation and properties are summarized in Table I.

FIGURE 3

EFFECT OF SURFACTANT ADDITIVE ON STRENGTH & QUALITY OF EPOXIDE-CURED, REINFORCED CNR-FILMS

MECHAN. PROPERTIES
TENSILE STRENGTH (psi) = ⊙————⊙
ELONGATION (%) = ⊙— — — —⊙

NOTES: CURATIVE WAS ERLC-4207 @
4.0 PPHR / CNR SOLIDS IN ALL CASES

CURE: EACH COAT WAS FORCE-DRIED
@ RMT & TEMPERED @
80°C X 15-30 MIN.

BUBBLE-FREE, TRANSPARENT FILM AT THIS ADDITIVE LEVEL

TENSILE STRENGTH (psi) & ELONGATION (%)

LEVEL OF ZONYL-A SURFACTANT ADDITIVE
(WEIGHT % OF TOTAL FORMULATION)

Table I

CNR-Gum Solvent Composition and Properties

CNR Gum (Batch A-021)	15.0
Hi-Sil 233	1.5
FC-77	34.0
HFX	25.5
Halocarbon-112A	17.0
Freon-113	8.5
Zonyl-A	0.051
ERLC-4207 (Curative)	0.6
Application	Brush
Viscosity (#5 Spndl/60 rpm)	260 cps 23°C
Working Life (ambient)	>2 weeks
Tack Free (force dried at RMT)	~10-15 min.

g.   Application Techniques

The CNR-Gum solvent composition prepared above was easily brushed onto a solvent-cleaned G-10 circuit board surface and a mold-release treated glass plate. The working life of the formulation exceeded two weeks at ambient temperatures (a minimum of 1 hour is required).

Preliminary attempts were made to apply this coating by air-spray techniques with only limited success. The solvent system described was developed for fast drying at room temperature (and rapid curing). This however leads to premature solvent loss in the atomizing air stream of conventional air-spray equipment causing cobwebbing or premature gellation of the polymer before levelling of the coating can take place on the substrate. This should not occur with airless spray equipment of either the pressurizing or electromagnetic vibrator types ... which were not available for this phase of the program.

A unit that has been reported to be effective for spraying urethane-based coatings at the MSFC Astronautics Laboratory is the "Zicon Spray Gun" using a hydrocarbon propellant for atomizing in lieu of air. A sample of this coating can be supplied to NASA if requested for evaluation with the Zicon spray equipment.

h.   Large Batch (27.6 lb.) Preparation

A quantity of the silica reinforced gum-solvent composition was required for the preparation of free films and circuit board conformal coatings to be used in the testing and critical property study. An amount was also needed to supply NASA for its subsequent work and to fulfill the contract requirement.

The formulation employed earlier is tabulated below for the preparation of 27.6 lbs. of composition based on 4.08 lbs. of CNR Gum (Thiokol Batch A-021), M.W. 570,000 (intrinsic visc. method) with an acid content of .57 mole % (based on termonomer acid in TFE-CF$_3$NO terpolymerization).

Table II

CNR-Gum Solvent Composition - Large Batch Preparation

	Recipe	% Total	lbs.	gms.
CNR Gum (Thiokol A-021)	15.0	14.80	4.080	1,850.
Hi-Sil 233	1.5	1.48	.408	185
FC-77 (3M Co. Fluoroether)	34.0	33.50	9.252	4,180
1,3-Di-(trifluoromethyl) benzene	25.5	25.10	6.940	3,135.
Halocarbon-112A (chlorofluorocarbon)	17.0	16.75	4.626	2,090.
Freon-113 (du Pont Co.)	8.5	8.37	2.313	1,045.
Total	101.5	100.0	27.61	12,485.

The CNR Gum and the Hi-Sil 233 were blended on a 12 in. rubber mill, equipped with water-cooled rolls. The blended mass was then milled for one hour on the mill and then cut into 1/8 in. strips. The strips were added gradually over a one-hour period to the four-part solvent mixture in a 12 liter flask. The flask was equipped with a reflux condenser, thermometer and a large teflon half-moon stirring blade. The mixture was then heated at 45-50°C for several hours to complete the homogenization of the mix. The product was a thick off-white suspension.

2.   Cured Free Films - Preparation, Evaluation and Testing

    a.   Preparation

        The coating solution was prepared from 50 gm. of the CNR gum-silica suspension (prepared above), 0.3 gm. of ERLC-4207 and 0.025 gm. (1 drop) of Zonyl A (du Pont Co.). The amount of the curative used was 4.0 pphr/CNR solids.

        The glass plates used had been treated with a fluorocarbon mold-release agent. The coating solution was brush-coated onto the glass plate and allowed to air dry at ambient temperature for two hours. Four applications were usually made and the coated plate was then placed in an oven maintained at 180°F for 16 hours. The cured films were transparent, flexible, tack free and light amber in color. Film thickness usually ranged from 5-6 mils.

    b.   Evaluation and Testing

        This section is devoted to the evaluation and testing program as it applies to cured free films. Due to time and scheduling limitations only the most critical tests were performed.

        (1)   Modulus of Rigidity

        Requirement: The modulus of rigidity shall not exceed 2000 psi @ -40°C.

        The prescribed method of test for "Low Temperature Stiffening of Rubber" is ASTM D-1043T (or the corresponding Method in Fed. Std. 601). Attempts to employ a Gehman or Clash-Berg apparatus were thwarted due to the limitations on sample thickness imposed by the methods.

        Transparent sample films of the CNR solution coating, prepared for general testing, were a maximum of 10 mils (0.010") in thickness. The calculation of "G" (modulus of stiffness) depends on a basic relationship between angle of twist and sample thickness or the ratio width to thickness. The tables of permissible thicknesses range from 35 to 125 mils (0.035-0.125"). Interpolation between increments listed (in these ranges) is permissible but extrapolation beyond the limits (0.035-0.125, Clash Berg or 0.060-0.110, Gehman method, is not permissible!

A less desirable but still valid alternative depends on the relationship between "E", Young's modulus (or modulus of elasticity at the proportional limit) and "G", the apparent modulus of rigidity:

$$E = 2G (1 + \lambda) \text{ ---- where } \lambda \text{ is Poisson's ratio.}$$

Assuming $\lambda \simeq 0.5$ (for soft rubbers), then:

$E \simeq 3G$ or $G = \dfrac{E}{3}$, thus it can be safely concluded that a compliant elastomer having a modulus of elasticity at yield not exceeding 6000 psi stress (at -40°C), will not exceed 2000 psi in modulus of rigidity at that temperature.

Values for E were determined from stress/strain curves on an Instron tester @ -40°C to -45°C and were reported as:

$$\left. \begin{array}{l} 2120 \text{ psi} \\ 2095 \text{ psi} \\ 2650 \text{ psi} \\ 2210 \text{ psi} \end{array} \right\} \text{ Ave.} = 2268 \text{ psi}$$

Since $G = \dfrac{E}{3}$, $\dfrac{2268}{3} = 756$ psi ave. (value for "G")

The apparent modulus of rigidity for the CNR-solution coating was about 750 psi @ -40°C.

(2) Flammability

A sample film strip was tested in accordance with NASA Crew Bay procedures (MSFC-Spec.-101, para. 4.5.1; upward propagation mode) for flammability in oxygen. The strip did not burn.

$$\left. \begin{array}{l} \text{(3) } \underline{\text{Dielectric Constant}} \\ \\ \text{(4) } \underline{\text{Dissipation Factor}} \end{array} \right\}$$

These results will be discussed concurrently and presented in tabular form. Tests were conducted on sample films 7 to 10 mils thick at Thermo-Physics Corp., Cambridge, Mass.

The coating submitted (viz. the CNR-solution coating) met the requirements for Dielectric constant at 1 KHz and 100 MHz but did not meet the requirement for dissipation factor (loss factor) at 1 KHz nor at 100 MHz.

In all cases a sample film dried @ 40°C (96°F), gave lower values than the original (undried) samples, the solution coating registering the lowest overall values, as shown in the table below:

Dielectric Constant and Dissipation Factor

		Films Cured but Not Pre-Dried		Films Dried @ 40°C	
Test Frequency		1 KHz	100 MHz	1 KHz	100 MHz
Dielectric Constant	Required Not >3.0 @ 1 KHz Not >2.5 @ 100 MHz	.2.22	2.09	2.11	2.00
Dissipation Factor	Not >0.005 @ 1 KHz Not >0.001 @ 100 MHz	0.014	0.015	0.0068	0.0044

It might be noted that these requirements are far more stringent than those ordinarily specified for conformal coating materials such as polyurethanes. For example, pure polystyrene which is considered to have a very low dissipation factor would not be better than 10^{-3} at 100 MHz.

(5) Hardness

Hardness measurements could not realistically be obtained on films having a maximum thickness of 10 mils. Earlier work with molded sheets of a similar CNR gum (cured with ERLC-4207 and reinforced with 10 pphr of Hi-Sil-233) indicate the hardness range to be 35 to 45, Shore-A for the solution coating.

(6) Compression Set

Likewise, compression set measurements could not be made on such thin films (using stacking techniques). Available data from molded sheets of a CNR gum similar to batch A-021 used in this program

(with the same curing system and reinforcement), ranged from 9.0 to 15.0% and should be the same for the CNR solution coating.

(7) Specific Gravity

Specific gravity of the CNR solution coating and related nitroso polymers ranges from 1.8 or 1.85 to ~1.95 owing to their high fluorine content (and must necessarily exceed 1.2 as required).

(8) Tear Strength

Tear strength for films of the CNR solution coating (because of the thickness limitation) can only be estimated from work with molded sheets. This should fall in the range of 120-160 lbs/in., Die-C.

(9) Tensile Properties

The average tensile properties of the CNR Solution coating are as follows:

Tensile Strength (psi): 840
Elongation (%)   : 800

(10) Viscosity

The viscosity of the CNR Solution coating was 260 cps (2.6 poises) with a Brookfield viscosimeter (#5 spindle/60 rpm @ 23°C).

(11) Application Life

Application life for the CNR-Solution coating is more than 2 weeks at 23°C.

3. Circuit Board - Conformal Coating

    a. Application

        The circuit boards with attached electronic components we.re wiped with toluene followed by isopropanol to remove mold-release agents and surface contaminants.

        The diepoxide curative and surfactant were added to the CNR-Gum composition just prior to use. To 50 gm. of the CNR-Gum silica suspension was added 0.3 gm. of ERLC-4207 (dicyclopentadiene diepoxide - Union Carbide Corp.) and 0.025 gm. (1 drop) of Zonyl A surfactant (du Pont Co.).

        Four coats of the coating solution were brush-applied with an interval of 2 hours between coats. Separate applications were made on the electronic components to improve filleting and encapsulation of the components. The boards were then cured at 80°C for 16 hours. The thickness obtained ranged from 3 to 4 mils. There was a minimum amount of bubbles encountered.

        The above boards were used in the tests on vibration, thermal cycling and thermal shock.

    b. Evaluation and Testing

        (1) Vibration Protection

            Standard test boards (received from NASA-MSFC) having mounted components were brush-coated with 4 to 5 mils of the CNR solution coating system; component leads were filleted to the board and also the six-lead test harness. All samples were cured at 80°C.

            Vibration tests were performed at Raytheon Corp. under the direction of Thermo-Physics Corp. of Cambridge, Mass., on two of the coated boards.

            These were mounted in test fixtures, bushed and supported as prescribed by the NASA technical monitor.

Vibration testing was performed along the three major axes at levels of 1, 25 and 50 G amplitudes as directed. Visual and electrical continuity checks were performed at each "G" level.

The units were tested separately, first vibrated along the two planar axes. Visual inspection indicated no loss of adhesion (of the coating) to either board or components. The appearance of tiny bubbles (<0.2 m.m. in diameter) was noted in several areas remote from the components and the harnesses. Several of the fillets of coating material containing scattered bubbles before the test, showed some enlargement (of the bubbles) afterward but careful examination of these regions showed no loss of adhesion because a layer of intact coating was found beneath each "bubble area". Electrical checks indicated no loss of continuity in these areas at any time.

The bubbles are believed to be air, entrapped during the brush-application of the coating.

In vibrating the boards along the z-axis (perpendicular to the plane of the board), amplification of the input "G" levels was experienced in those regions (of the board) spanning the distances between the securing bolts. The amplification factor ran as high as 20 X the intended amplitude in some cases (viz.; the actual "G"-level was as high as 800-1000 G at an input of 50 G).

Visual inspection disclosed no loss of adhesion and electrical checks, no loss in continuity except as follows ----

"one of the six leads in the wire harness broke at the point of connection to the board after having survived the 50 "G" test in the other two axes".

Electrical tests of the components were performed before and after the vibration checks. Although the identities of the mounted components could not be provided by the NASA Astronautics Laboratory, it was determined by Thermo-Physics that two were resistors and their resistances were measured with a Wheatstone Bridge; two were diodes which were checked for forward conduction at 1.5 volts and reverse blocking at 6 volts; one proved unidentifiable and was checked for a blocking voltage of 6 volts in both directions.

These results are summarized in the table below:

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Electrical Checks of Mounted Components in the Vibration Test

Black lead to:	Before Vibration	After Vibration
Brown lead and resistor	34, 600 ohms	No change; all test results identical before and after vibration test.
Red lead and diode	blocks 6 volts -- conducts, red to black	
Orange lead and resistor	34, 700 ohms	
Yellow lead (component unidentified)	blocks 6 volts in both directions	
Green lead and diode	conducts blocks 6 volts, green to black	

In summary, both test boards appeared to have passed the vibration test. The one broken lead that was noted after the final cycle in the z-axis at 50 "Gs" must be discounted after considering that the amplification factor in this direction was at least 20 X (resulting in a real amplitude of 800-1000 "Gs").

(2) Thermal Cycling Protection

Several "test pattern" circuit boards bearing soldered components were coated with the CNR solution system to a thickness of approximately 4 to 5 mils and cured at about 80°C. The boards were subjected to 10 thermal cycles (-65°C to room temperature to 100°C, each cycle). No evidence of cracked solder joints, blistering, loss of adhesion or other failure mode was observed.

(3) Thermal Shock Cycle

The circuit boards from the above test were then subjected to one thermal shock cycle (-65°C to 100°C) in accordance with procedures in the contract. No evidence of any type of failure was apparent after careful examination. These boards were submitted to the Technical Monitor at NASA-MSFC for further evaluation.

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(4) Adhesive Bond Strength

Style 181 and HG-84 glass fabrics were bonded in 2 inch wide strips to G-10 circuit board with the CNR solution coating (brushed through the fabric) and cured under light clamping pressure at 80°C. The fabric was slit down to the G-10 substrate to form 1 inch wide panel strips. These were peeled on an Instron Tester at a 2 inch/min. crosshead speed. The strength of the bonds formed was apparent from the fact that the glass fabric tore each time between 6 and 8 lbs./inch width but the adhesive did not fail. In one instance a load of close to 10 lbs./in. was reported before the fabric tore.

B. Liquid Prepolymer Development

This development is concerned with the preparation of a solventless liquid system consisting of a liquid prepolymer and the requisite curative leading to a highly reliable conformal coating. The approach taken deals with the synthesis of liquid nitrosofluorocarbon prepolymers of the desired application viscosity with the proper range of functionality, reactive groups and curing characteristics. Functional groups capable of serving as cure sites are those possessing active hydrogen atoms such as carboxyl, hydroxyl and amide groups. The program has been directed towards carboxyl functioned material and the hydroxyethyl ester prepared therefrom by means of ethylene oxide.

1. Carboxyl Functional Nitrosofluorocarbon

The synthesis program has been directed towards the preparation of low molecular weight carboxyl containing nitrosofluorocarbon polymers of the structure below possessing a dynamic viscosity in the vicinity of, but less than, 250 poises.

$$-\underset{\underset{\underset{COOH}{|}}{(CF_2)_a}}{\overset{|}{N}}-O-CF_2CF_2-\left[\underset{\underset{CF_3}{|}}{\overset{|}{N}O}-CF_2CF_2\right]_n-\underset{\underset{\underset{COOH}{|}}{(CF_2)_a}}{\overset{|}{N}}-O-CF_2CF_2-$$

The above generalized terpolymer, where "a" is 3, may be prepared from CF_3NO, C_2F_4 and nitrosoperfluorobutyric acid. In other instances the value of "a" may be 1 depending on the synthesis routes.

The molecular weight range sought in these efforts covered the range of 2,000 to 4,000 for the most part.

The carboxy nitrosofluorocarbons present a group of materials amenable to cure via reaction with diepoxides. The chemistry of the cure reaction had been depicted earlier in the section dealing with CNR cures with diepoxides.

Several approaches had been utilized in the synthesis program aimed at carboxyl functioned polymers. They are described in the following sections.

a. Liquid CNR

(1) Synthetic Programs

(a) Chlorine-Freon 113 Modified Terpolymerization

The achievement of a liquid terpolymer from the terpolymerization of tetrafluoroethylene, nitrosotrifluoromethane and nitrosoperfluorobutyric acid depends on modification of the conventional -40°C methylene chloride polymerization. The usual product is a rubbery gum of high molecular weight.

The participation of polymerization solvents as chain termination agents had been described by Crawford (Ref. 1). The use of solvents containing chlorine resulted in polymers of lower molecular weight than that obtained in perfluorinated solvents.

In addition to the solvent role, Thiokol Chemical Corp. research had found that the addition of elementary chlorine resulted in liquid low molecular weight polymers of high viscosity by virtue of the chain transfer mechanism provided thereby.

The use of Freon 113 as a chain modifier in the absence of chlorine resulted in the formation of a gum polymer. This points out the need for both chlorine and Freon 113 in arriving at liquid polymers.

The employ of chlorine as a chain modifier in Freon 113 at -25°C has been further extensively examined for the terpolymerization of tetrafluoroethylene, trifluoronitrosomethane and nitrosoperfluorobutyric acid. Freon 113 has been shown to be preferred to

methylene chloride since the latter solvent yielded a liquid with a viscosity of 277 poises as against 185 poises for the use of Freon 113 (see Runs 3 and 4 in Table III).

The amount of chlorine employed in these experiments ranged from 2.5 to 10.0 mole %. As expected the use of increased chlorine gave rise to lower viscosity polymers. The use of minimal amounts of chlorine gave rise to higher viscosity polymers. Table III supplies information on this point.

In the polymerization performed the ratio of fluoro-olefin to nitroso components was 1.1:1.0 in most instances.

The amount of nitrosoperfluorobutyric acid has been varied from 6.0 to 10.0 mole % of total monomers. The use of 6.0-7.5 mole % of nitrosoacid produced lower viscosity liquids than the 10 mole % polymerizations.

Polymerization runs conducted through Run 14 were on a 1 mole scale. Those runs from Run 18 through 28 were on a 2 mole scale. The solvent in the 1 mole runs was 300 gm. Freon 113 per mole. That of the 2 mole runs was 250 gm. Freon 113 per mole. The polymerization vessel used in each instance was a 1600 ml. Fischer-Porter heavy walled glass cylinder equipped with an aerosol compatibility valve and coupling. The temperatures ranged in the vicinity of -25°C. Shaking was maintained for 48 hrs. at -25°C in a refrigerated bath. The cold contents were vented and allowed to reach room temperature. The solvent was removed at atmospheric pressure up to 80°C. The contents were then gradually brought to 100°C at 0.1 mm in a nitrogen atmosphere. The volatile portion usually contained some residual nitrosoperfluorobutyric acid and oxazetidine. The conversions were excellent and in most instances exceeded 90%.

The carboxyl analysis of the polymers is given in Table III as m.e.q./gm. based on a titration of 0.4 to 0.5 gm. in 25 ml. of Freon 113 with .02 N di-n-butyl amine in Freon 113 with bromcresol green indicator (Ref. 2).

The viscosities were obtained using a Gardner Bubble Viscometer. The kinetmatic viscosity obtained therefrom in stokes was multiplied by 1.87 (density of the various carboxylic nitrosofluorocarbon polymers) to reach the value is poises reported in Table III. The viscosities obtained cover a wide span of values.

The infrared spectrum of a typical chlorine modified carboxyl terpolymer is shown in Fig. 4. The carbonyl of the carboxyl is evident at 5.6μ. The hydrogen of the carboxyl function is characterized by the broad absorption at 2.8-3.5μ.

The range of equivalent weights of the liquid polymers synthesized covers the span of 1200 to 2000.

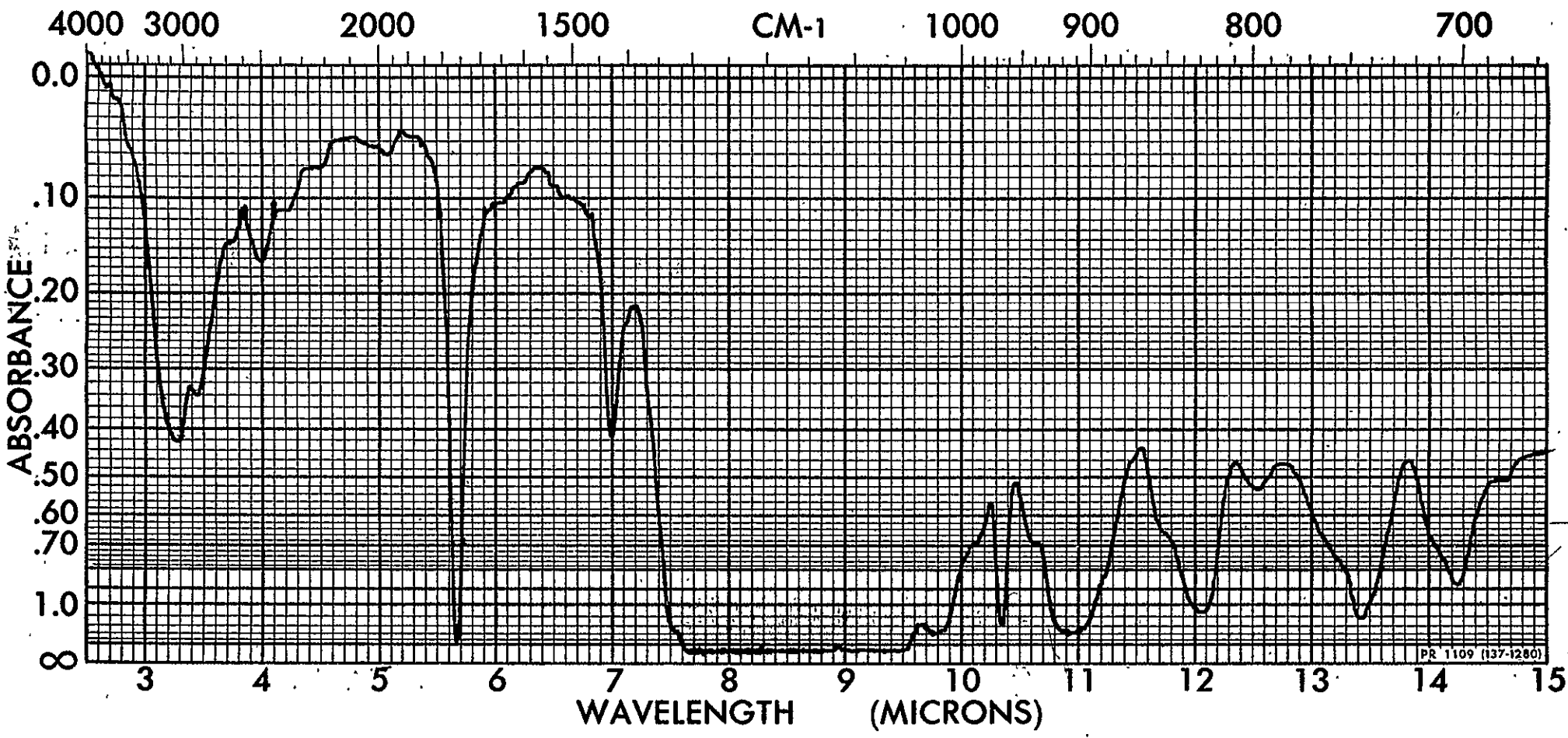Fig. 4. Infrared Spectrum of a Typical Carboxy Nitrosofluorocarbon Polymer

Table III

Chlorine-Freon 113 Modified Terpolymerizations

Polym. Run	Mole % Acid	Mole % Chlorine	Viscosity (Poises)	Carboxyl m. e. q. /gm.	Yield
1	10	0	Gum	-	82
2	10	10	20	.86	73
3	10	5	185	.83	75
4*	10	5	277	.80	96
12	10	5	184	.79	90
14	7.5	5	94	.61	86
18	10	5	151	.79	91
19	7.5	5	68	.60	92
20	6.0	5	38	.47	94
21	7.5	5	56	.59	92
22	6.0	5	38	.49	92
23	7.5	2.5	262	.60	90
24	6.0	2.5	337	.50	92
25	6.0	3.75	56	.56	75
26	7.5	3.75	112	.60	90
28	10.0	5.0	150	.74	93

*Performed in methylene chloride.

(b) Bromotrichloromethane-Freon 113 Modified Terpolymerization

Bromotrichloromethane was selected for study as a modifier in the terpolymerization of tetrafluoroethylene, trifluoronitrosomethane and nitrosoperfluorobutyric acid. The objective was a low molecular weight liquid carboxylic polymer with a viscosity less than 250 poises.

The choice of bromotrichloromethane as an alternate chain modifier was made since it would be expected to lead to free radicals capable of terminating polymer chains. The radicals formed would presumably be bromo and trichloromethyl radicals resulting from the attack of polymer free radical intermediates. Thus:

$$\left(\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_3 \end{array}\right)_x \begin{array}{c} N-OCF_2CF_2\cdot \\ | \\ CF_3 \end{array} + BrCCl_3 \longrightarrow \left(\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_3 \end{array}\right)_x \begin{array}{c} N-OCF_2CF_2Cl \\ | \\ CF_3 \end{array}$$

$$+ \cdot CCl_3$$
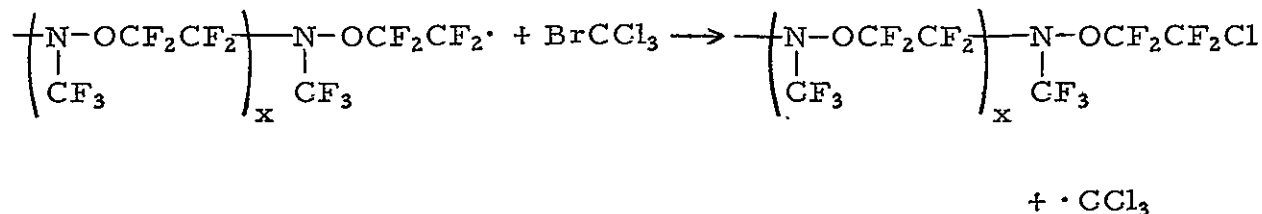
The trichloromethyl radical would be free to terminate another polymer radical chain.

Polymerization Run No. 8 was performed at $-25°C$ in Freon 113 using 10 mole % nitrosoperfluorobutyric acid, 50 mole % tetrafluoroethylene and 40 mole % nitrosofluoromethane and 5 mole % bromotrichloromethane as chain modifier. The product was a straw-colored thick oil with a viscosity of 28 poises and a carboxyl titre of .800 m.e.q./gm. The utilization of 84% of the applied nitrosobutyric acid was noted. The yield of carboxylic nitrosofluorocarbon polymer achieved was 94% of theory. The work-up of the material involved removal of Freon 113 followed by vacuum stripping at $85°C$ and 0.1 mm to remove any unreacted nitrosobutyric acid, low boilers and oxazetidine.

The infrared spectrum reported in Figure 5 is characteristic for a nitrosofluorocarbon possessing carboxyl functions. The carbonyl of the carboxyl was evident at 5.65μ and that of the active hydrogen of the carboxyl noted at 2.8 to 3.5.

Polymerization Run No. 9, performed as a duplicate of Run No. 8, employing bromotrichloromethane, led to a translucent gum of very low mobility which darkened extensively on heating at reduced pressure.

This approach was not studied further in view of the success obtained with the use of chlorine and Freon 113 as chain modifiers.

(2) Curing Agents

Diepoxides offer an opportunity for cure reactions with di- and poly-carboxylic nitrosofluorocarbons. Where a strictly difunctional acid is used the product would be a polymer resulting from chain extension. A functionality greater than two would lead to an amount of crosslinking.
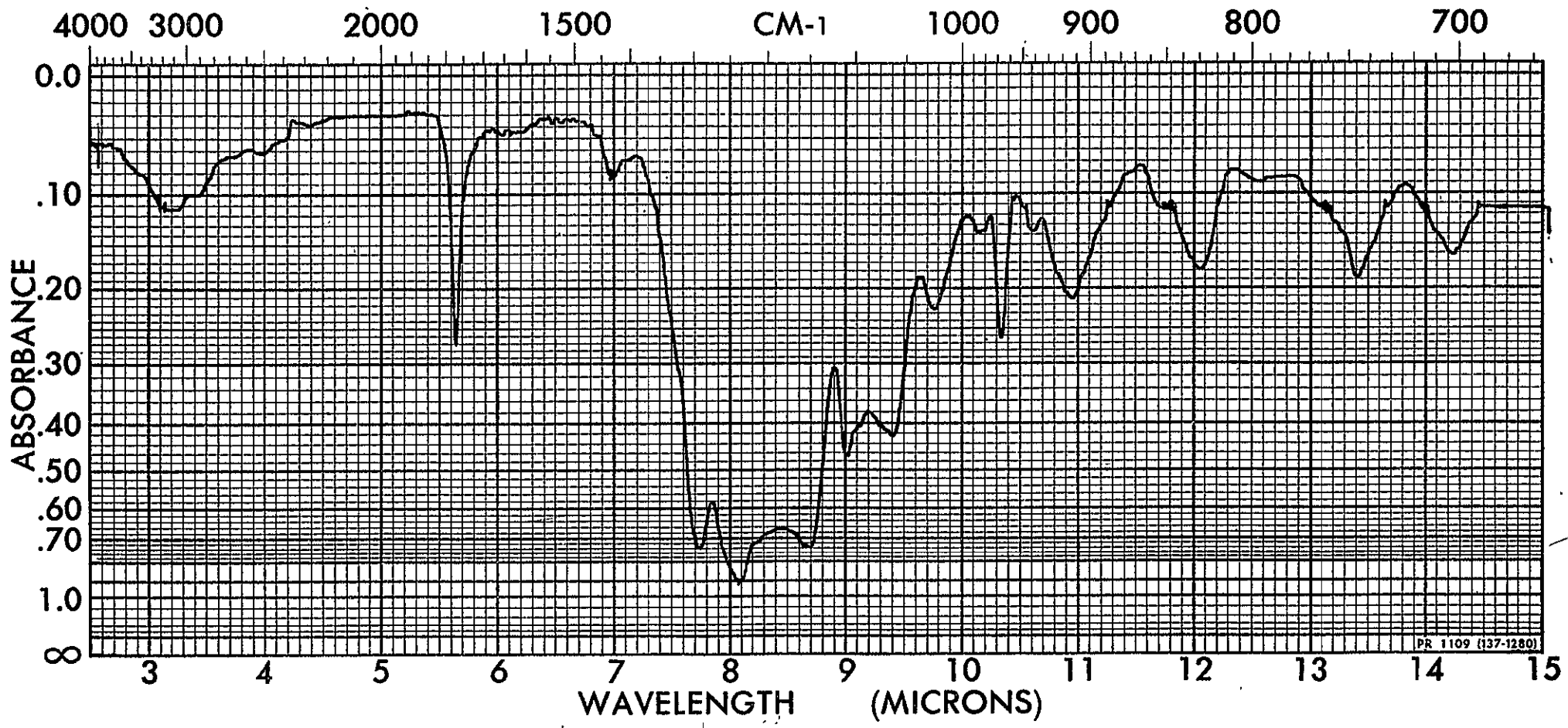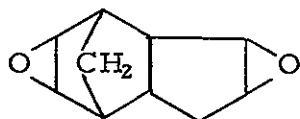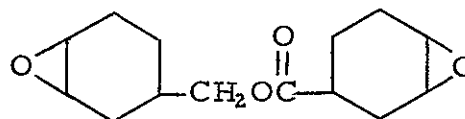
Fig. 5. Infrared Spectrum: Polymer Run No. 8 - Bromotrichloromethane Modified Carboxylic Nitrosofluorocarbon
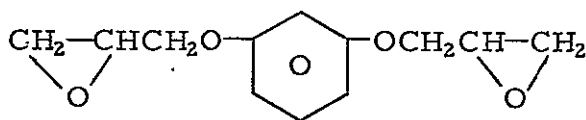
The various diepoxides selected for study are shown below. The diepoxide which received major interest was ERLC-4207, produced by Union Carbide.

ERLC-4207 (Union Carbide)

ERLA-4221 (Union Carbide)

ERE-1359 (Ciba)
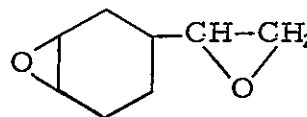
RD-4 (Ciba)

(3) Cup Cures

The various liquid polymers prepared above (Table III) were subjected to 1 to 2 gm. cup cures as indicated below. The curing agent which showed the best applicability in terms of clarity, moderate rate of cure and completion of cure was ERLC-4207. The amount of curing agent found most useful was a 10 to 20% excess over the carboxyl titre of the functional polymer. In many instances the "brush life" of the mixture exceeded 30 minutes.

(a) Polymer No. 12 Products

1) ERLC-4207; 1 equivalent of curative produced a clear mix which thickened with time. After 25 min. it gave a slight flow, after 1 hour it was extremely thick. After 1 hour at ambient temperature the mix was heated at $180°F$. A pale yellow tack-free disk was obtained of good transparency.

2) ERE-1359; 1 equivalent of curative produced an almost complete rapid cure in 12 minutes. After 1 hour at ambient temperature the mixture was heated at $180°F$ to give a crumbly amber solid.

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3)   RD-4; 1 equivalent of curative immediately produced a white opaque mass with foaming and rapid cure to a white solid. Heating at 180°F gave a white mass which crumbled easily.

(b)   Polymer No. 14 Products

1)   ERLC-4207; 1 equivalent of curative produced a clear mix with gradual thickening. Excellent mobility after 1 hour. A cure at 180°F for 16 hours gave a transparent, pale yellow disk tack-free and flexible. The use of .5 equivalent of curative gave a fair cure with some tack.

(c)   Polymer No. 18 Products

1)   ERLC-4207; the curative was applied at levels of 90, 100 and 110% of an equivalent. The brush life varied from 1/2 to 1 hour. The 90%-curative cured at 180°F to give a pale yellow disk with slight tack. The 100 and 110%-curative products cured at 180°F to give tack-free disks.

(4)   Film Cures

The various liquid polymers prepared above (Table III) were subjected to 5 to 10 gm. film cures on mold-release treated glass plates, as indicated below. The curing agent employed was ERLC-4207. The amount of agent found most useful was a 10 to 20% excess over the carboxyl titre of the functional polymer. In many instances the leveling was very good and cured films were obtained with high transparency, tack-free and good flexibility.

(a)   Polymer No. 12 Products

1)   ERLC-4207; to 5 gm. of polymer was added 0.33 g. of curative (100% of theory) and mixture poured after 30 minutes onto a 3 x 4 in. glass plate (release-treated). The mixture leveled fairly well and was after 2 hours placed in oven at 180°F for 16 hours. Film was pale yellow, transparent, flexible, tack-free and 12-16 mils in thickness. Tensile' strength was 150-185 psi at 100% elongation.

2) ERLC-4207; the use of .5 wt. % 2-ethyl hexanoic
was applied to the above recipe 1) to examine retardation of cure. The
ening in the first 30 minutes was comparable to the above. Films were
ned which were pale yellow, transparent, flexible and tack-free. The
le strength with 175-210 psi at 100% elongation.

(b) Polymer No. 14 Products

1) ERLC-4207; to 5 gm. of polymer was added
5 g. of curative (100% of theory) and mixture poured after 15 minutes
a 3 x 4 in. glass plate (release-treated). The mixture leveled well.
: 2 hours placed in an oven at 180°F for 16 hours. Film was pale yellow,
sparent, flexible and tack-free. Tensile strength was 140-150 psi at
120% elongation.

(c) Polymer No. 18 Products

1) ERLC-4207; to 10 gm. of polymer was added
g. (110% of an equivalent) of curative. The liquid was poured onto a
4 in. glass plate (Teflon release-coated). The mixture leveled well
ng 2 hours at ambient. Cure at 180°F for 16 hours gave an amber film of
!5 mils thickness, tack-free, flexible and relative bubble-free. Tensile
·ngth 170-180 psi at 50% elongation.

(d) Polymer No. 19 Products

1) ERLC-4207; to 10 gm. of polymer was added
gm. (110% of an equivalent) of curative. The liquid was brushed out onto
x 4 in. glass plate (Teflon release-coated). The mixture leveled well.
·e at 180°F for 16 hours gave an amber film, flexible, and possessing very
le tack.

(e) Polymer No. 20 Products

1) ERLC-4207; to 10 gm. of polymer was added
)% of an equivalent of curing agent and mixture brushed onto a 4 x·4 in.
:a on a release-treated glass plate. Brush life estimated at 50 minutes.
re at 180°F gave a transparent, flexible film exhibiting some residual tack.

(f)   Polymer No. 21 Products

1)   ERLC-4207; levels of 90%, 110% and 120% of an equivalent of agent were added to 10 gm. of polymer and the mixture brushed onto a 4 x 4 in. area on a release-treated glass plate. Brush life approximated 40 minutes. Cure at 180°F for 16 hrs. gave transparent, flexible film. The 120% level product possessed no tack and had a tensile strength of 125-140 psi and an elongation of 100%.

(g)   Polymer No. 22 Product

1)   ERLC-4207; a level of 110% of an equivalent of agent was added to 10 gm. of polymer and the mixture brushed onto a 4 x 4 in. release-treated glass plate. Cure at 180°F for 16 hrs. gave a transparent, pale yellow, flexible film possessing slight tack.

(h)   Polymer No. 24 Product

1)   ERLC-4207; a level of 110% of an equivalent of agent was added to 10 gm. of polymer and the mixture brushed onto a 4 x 4 in. release-treated glass plate. Cure at 180°F for 16 hrs. gave a transparent, light amber, flexible film with no tack. Tensile strength was 45-50 psi and had an elongation of 50%.

(i)   Polymer No. 8 Product (BrCCl₃ Modified Terpolymer)

1)   ERLC-4207; to 10 gm. of polymer was added .73 gm. (110% of an equivalent) of curative. The liquid mixture thickened slightly after 1 hour. Brushed onto a 4 x 4 in. glass plate (Teflon release-coated). Cure at 180°F for 16 hours gave a pale yellow film which was tacky on the surface close to glass plate.

(5) Film Evaluation and Testing

(a) Transparency

Cured films in the range of 10-30 mils, prepared above, were easily transparent. Several layers amounting to 100 mils in thickness, from Polymer No. 24 and 110 equivalent % of ERLC-4207, was transparent.

(b) Flammability

A sample of film was not flammable at an oxygen pressure of 32 lbs. when exposed to a glowing wire at upward propagation. Combustion did not occur when the film was exposed to a burning piece of paper held below the film in an oxygen atmosphere.

(c) Dielectric Constant

(d) Dissipation Factor

These results will be discussed concurrently and presented in tabular form. The tests were conducted on a 20 mil film from Polymer Run No. 18 and 110 equivalent percent of ERLC-4207 curing agent. The data was obtained from the Thermo-Physics Corporation, Cambridge, Mass.

The coating met the requirement for dielectric constant at 1 KHz and 100 MHz but did not meet the requirement for dissipation factor (loss factor) at 1 KHz nor at 100 MHz.

When the sample film was dried at 40°C it gave lower values than the original (undried) sample. The data is shown:

	As received		After 72 hours at 40°C	
Test Frequency	1 KHz	100 MHz	1 KHz	100 MHz
Dielectric Constant	2.32	2.05	2.19	2.05
Dissipation Factor	0.0203	0.0069	0.0131	0.0067

The requirement for the dielectric constant is that it not exceed 3.0 at 1 KHz and shall not exceed 2.5 at 100 MHz.

The requirement for the dissipation factor is that it not exceed 0.005 at 1 KHz and shall not exceed 0.001 at 100 MHz.

It might be noted that these requirements are far more stringent than those ordinarily specified for conformal coating materials such as polyurethanes. For example, pure polystyrene which is considered to have a very low dissipation factor would not be better than 10^{-3} at 100 MHz.

(e) Adhesion

An amount of liquid polymer No. 21 (2 gm.) was treated with 110% of an equivalent (.11 g.) of ERLC-4207 diepoxide. The liquid was applied to a solvent-cleaned G-10 circuit board over a 2 x 3 in. surface. Cure at 180°F for 16 hours ensued. The adhesion was excellent and the film could be dislodged with difficulty by means of a razor blade.

(f) Specific Gravity

The specific gravity of the liquid carboxylic nitrosofluorocarbon polymers was in the range of 1.87 to 1.89.

(g) Viscosity

The viscosity range of the liquid polymers shown in Table III lies for the most part between 50 and 250 poises.

Complete stability to viscosity change was exhibited by the liquid polymers over a period of a month.

(h) Application Life

The brush life of many of the liquid polymer-ERLC-4207 mixtures exceeded 30 min. to 1 hr. Good leveling on a glass surface was noted with these mixtures.

The retarding effect of .1 to .5 wt. % (based on polymer) of 2-ethylhexoic acid may serve to increase the application life of the formulated cure blend.
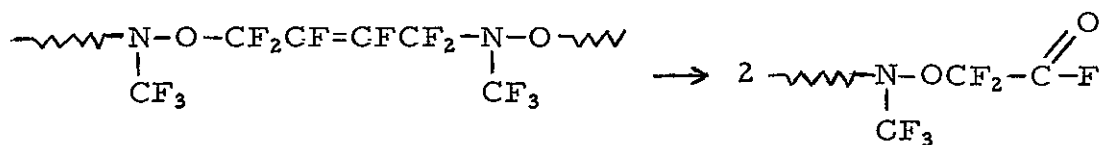
(i) Tensile Properties

ERLC-4207 diepoxide cured films were obtained with the polymers shown below along with tensile strengths and % elongations.

Cured Polymer No.	Tensile (psi)	% Elongation
12	150-185	100
14	140-150	100-120
18	170-180	50
21	125-140	100
24	45-50	50

b. Synthesis from Unsaturated Terpolymers

The utilization of unsaturated nitrosofluorocarbon polymers (Ref. 3, 4 and 5) holds considerable promise in the synthesis of carboxylic materials. Unsaturated terpolymers produced from tetrafluoroethylene, nitrosotrifluoromethane and hexafluorobutadiene have served in this area. The oxidation of the unsaturated group via ozone under pressure had been demonstrated by an earlier Thiokol investigation (Ref. 3). The extension of this program to lead to products of more sutiable viscosity and greater utilization in cure reactions was one of the goals of the present work.

The attack on an unsaturated site via the action of ozone to give an acyl fluoride may be represented thus:

$$\text{--}\wedge\wedge\wedge\text{--N--O--}CF_2CF{=}CFCF_2\text{--N--O--}\wedge\wedge\wedge \quad \underset{CF_3}{\overset{}{|}} \qquad \underset{CF_3}{\overset{}{|}} \quad \longrightarrow \quad 2 \ \text{--}\wedge\wedge\wedge\text{--}\underset{CF_3}{\overset{}{\underset{|}{N}}}\text{--O}CF_2\text{--}\overset{\displaystyle O}{\overset{\|}{C}}\text{--F}$$

The polymeric acyl fluoride has been shown to readily undergo hydrolysis in a Freon 113-water suspension at room temperature to give the corresponding carboxylic acid.

(I) <u>Preparative Procedure</u>

The initial step in this proposed synthesis is the preparation of the gum terpolymer, $CF_3NO/C_2F_4/CF_2=CF-CF=CF_2$ (Ref. 3, 4 and 5). Thus:

$$(a + b) \; CF_3NO + a \; CF_2 = CF_2 + b \; CF_2=CF-CF-CF_2 \longrightarrow$$

$$\left[\begin{matrix} N-OCF_2CF_2 \\ | \\ CF_3 \end{matrix}\right]_a \left[\begin{matrix} N-OCF_2CF = CFCF_2 \\ | \\ CF_3 \end{matrix}\right]_b$$
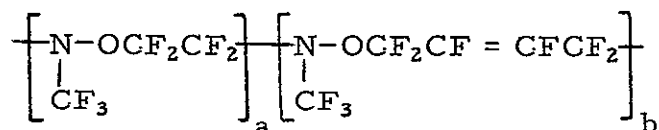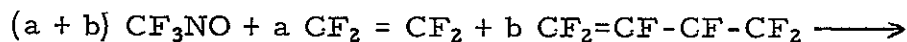
The structure shown is that for the terpolymer possessing backbone unsaturation and is accompanied by pendent unsaturation as well. The ratio of pendent to backbone unsaturation is 1:7 (Ref. 5). Ozonolysis of the prod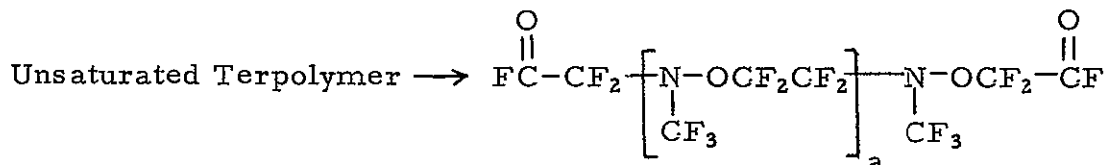uct has been shown to attack preferentially the backbone unsaturation and form the respective polymer acyl fluoride with a functionality of 2. Thus:

$$\text{Unsaturated Terpolymer} \longrightarrow \overset{O}{\overset{||}{FC}}-CF_2\left[\begin{matrix} N-OCF_2CF_2 \\ | \\ CF_3 \end{matrix}\right]_a N-OCF_2-\overset{O}{\overset{||}{CF}}$$

Amounts of the unsaturated terpolymer were prepared using 7.5 mole % (Polymer Run No. 10) and 5.0 mole % (Polymer Run No. 15) of hexafluorobutadiene. Freon 113 is preferable to methylene chloride as the solvent since the product is obtained in solution, amenable to the subsequent ozonolysis reaction. Thus, Run No. 10, performed in methylene chloride yielded the product as a gummy deposit. The product of Run No. 15 was obtained in Freon 113 solution. The one mole scale terpolymerizations were conducted at -40°C to -45°C over a 6-day period in a 1600 ml. Fischer-Porter heavy-walled vessel. The vessel was agitated in a refrigerated bath. An amount of 300 gm. of solvent was used. The solvent was deaerated by the freeze-thaw technique.

The unavailability of commercial ozone-Freon 13 solution, due to difficulties of the manufacturer, made it imperative that gaseous ozone, produced in a laboratory ozonizer be examined in its stead. The previous work (Ref. 5) had indicated that liquid ozone-Freon 13, under pressure, was to be preferred to atmospheric ozone. It has now been found

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that continuous passage of excess gaseous ozone through a 20% solution of the unsaturated polymer in Freon 113 at 10-15°C accomplished cleavage of both types of double bonds in the polymer. Infrared examination of the samples during the ozonolysis indicated ready loss of the backbone unsaturation, noted at 5.82μ and gradual diminution of pendent unsaturation at 5.65μ. Formation of acyl fluoride was evidenced by COF absorption at 5.35μ.

Hydrolysis of the acyl fluoride functions of the ozonized polymer yields the corresponding terminal dicarboxylic acid of the nitrosofluorocarbon polymer. The yield of viscous liquid polymer was in the vicinity of 60% based on the original monomer charge.

Table IV lists the data on the runs performed yielding terminal dicarboxylic acid polymers.

Table IV

Ozone-Hydrolysis Products from Unsaturated Terpolymers

Polymer Run	Hexafluorobutadiene (mole %)	Viscosity (Poises)	m. e. q. /gm.	Yield %
10	7.5	240	1.90	60 ca.
15	5.0	150	.67	60 ca.

The infrared spectrum of the product of the ozonolysis-hydrolysis of the unsaturated terpolymer from Polymer Run No. 10 is typical of a carboxylic nitrosofluorocarbon and is given in Fig. 6.

(2) Cure Reactions

Cup cures were investigated with Polymer Run No. 10 carboxylic acid and curatives (a) ERLC-4207, (b) ERLA-4221, (c) ERE-1359, and (d) RD-4. In each instance a very rapid cure ensued in several minutes to give white opaque products.

In similar fashion, Polymer Run No. 15 carboxylic acid gave a very rapid cure with ERLC-4207 yielding an opaque white disk.
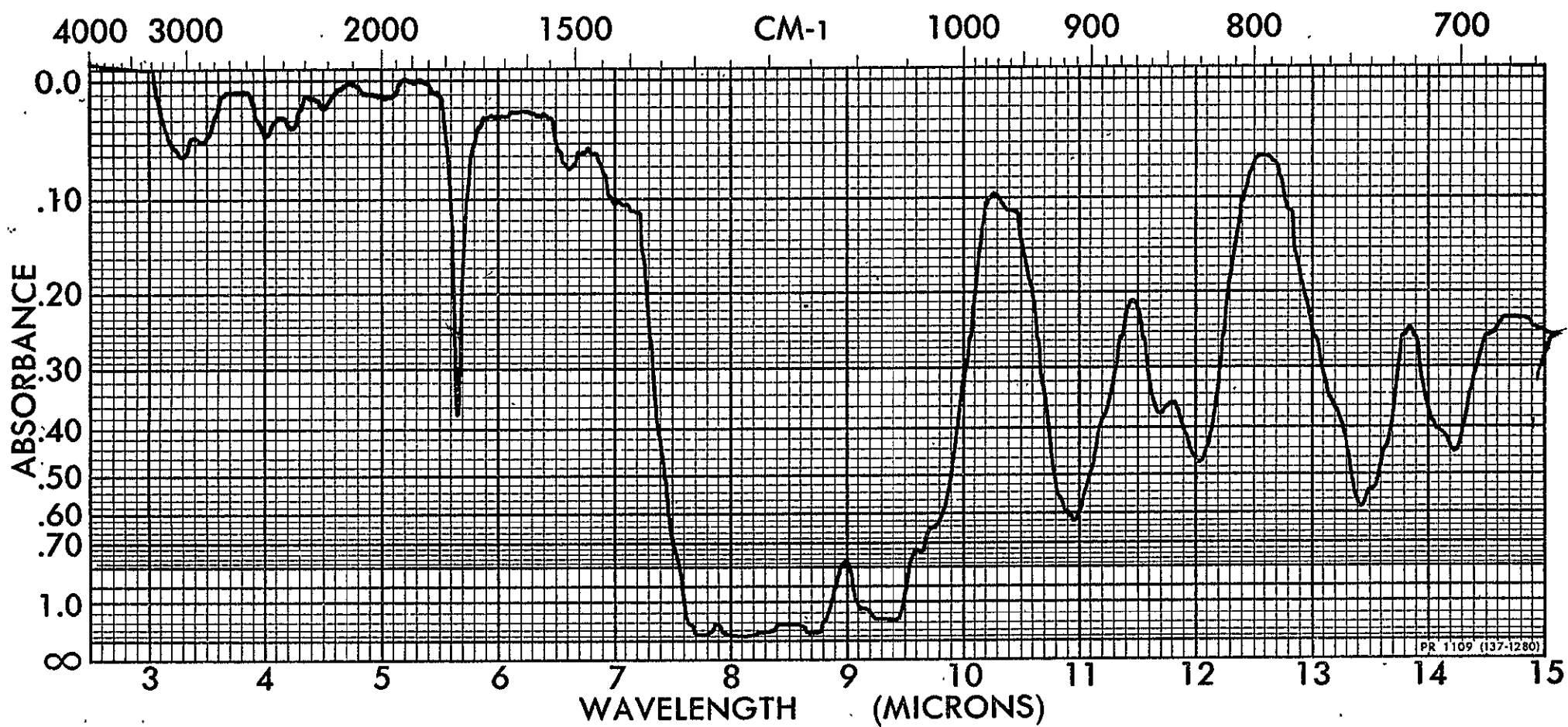
Fig. 6. Infrared Spectrum of Carboxy Nitrosofluorocarbon Polymer
from Terpolymer Ozone-Hydrolysis

It appears that the terminal dicarboxylic acids prepared above are more energetic than the chain modified liquid CNR products. This places a limitation on the use of these terminal dicarboxylic polymers.
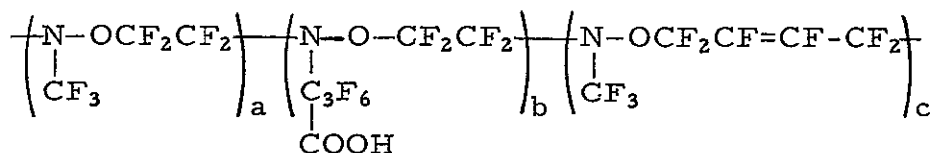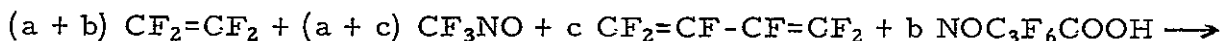
c.   Synthesis from Unsaturated Carboxylic Tetrapolymers

The ozonolysis of the unsaturated terpolymer as reported above is expected to give a terminal dicarboxylic and with a functionality of two. Cure reactions with a diepoxide would be solely chain extending in nature with these products.
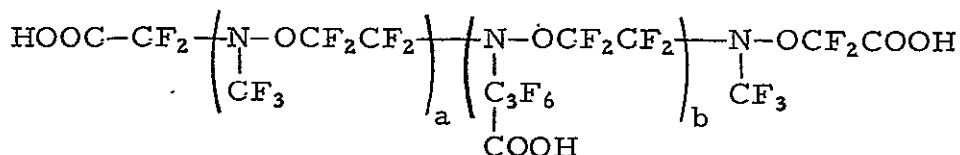
It was therefore considered of interest to provide a functionality greater than two in a polymer to promote a degree of crosslinking in addition to chain extension on reaction with a difunctional curative.

A proposed route to carboxylic acid polymers with a functionality greater than two is suggested by the preparation of an unsaturated carboxy nitrosofluorocarbon polymer and its subsequent ozonolysis.

The formation of a tetrapolymer would be based on the incorporation of an amount of nitrosoperfluorobutyric acid in the usual unsaturated terpolymer recipe. Thus:

$$(a + b) \ CF_2{=}CF_2 + (a + c) \ CF_3NO + c \ CF_2{=}CF{-}CF{=}CF_2 + b \ NOC_3F_6COOH \longrightarrow$$

$$\left(\begin{array}{c} N{-}OCF_2CF_2 \\ | \\ CF_3 \end{array}\right)_a \left(\begin{array}{c} N{-}O{-}CF_2CF_2 \\ | \\ C_3F_6 \\ | \\ COOH \end{array}\right)_b \left(\begin{array}{c} N{-}OCF_2CF{=}CF{-}CF_2 \\ | \\ CF_3 \end{array}\right)_c$$

Ozonolysis-hydrolysis of the above unsaturated carboxylic polymer is expected to proceed thus:

$$HOOC{-}CF_2 \left(\begin{array}{c} N{-}OCF_2CF_2 \\ | \\ CF_3 \end{array}\right)_a \left(\begin{array}{c} N{-}OCF_2CF_2 \\ | \\ C_3F_6 \\ | \\ COOH \end{array}\right)_b N{-}OCF_2COOH \\ | \\ CF_3$$

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(1) Preparative Procedure

A series of three tetrapolymerizations were conducted using levels of hexafluorobutadiene of 2, 4 and 7.5 mole % at a constant 2 mole % of nitrosoperfluorobutyric acid. The polymerizations were carried out in Freon 113 at -25°C over a six-day period. The infrared spectrum of the unsaturated tetrapolymer is shown in Fig. 7, with absorption at 5.65 for carbonyl and pendent unsaturation, 5.82 for backbone unsaturation and 2.8-3.5 for carboxylic acid hydrogen.

Ozonolysis of the unsaturated tetrapolymer with excess atmospheric gaseous ozone at 10-12°C over a 10-hour period gave a product containing acyl fluoride. This is evidenced by Fig. 8 showing a new absorption at 5.3 for acyl fluoride and absence of backbone unsaturation (noted in Fig. 4 at 5.82). Hydrolysis of the above product with water at room temperature for 24 hours gave rise to a polycarboxylic acid. The infrared spectrum is shown in Fig. 9 and is characteristic for a carboxylic nitrosofluorocarbon. Table V lists the products with viscosity and carboxyl titre values.

Table V

Ozone-Hydrolysis Products from Unsaturated Tetrapolymers

Polymer Run	Hexafluorobutadiene (mole %)	Nitrosoacid (mole %)	Viscosity (Poises)	m.e.q./gm.	Yield %
13	7.5	2.0	280	1.09	60 ca.
16	4.0	2.0	280	.59	64 ca.
17	2.0	2.0	277	.46	72 ca.

The viscosity of the above three products is in slight excess of the 250 poises sought in this program. The carboxyl titre obtained presents a good range for examination in dieepoxide cure reactions. The products were viscous oils possessing a slight haziness.

(2) Cup Cures

Cup cures were conducted with the carboxylic acid polymers derived from the ozonolysis-hydrolysis of the unsaturated carboxylic nitrosofluorocarbon polymers. These products gave clear, transparent mixes of moderate cure rate in great contrast to the products from the
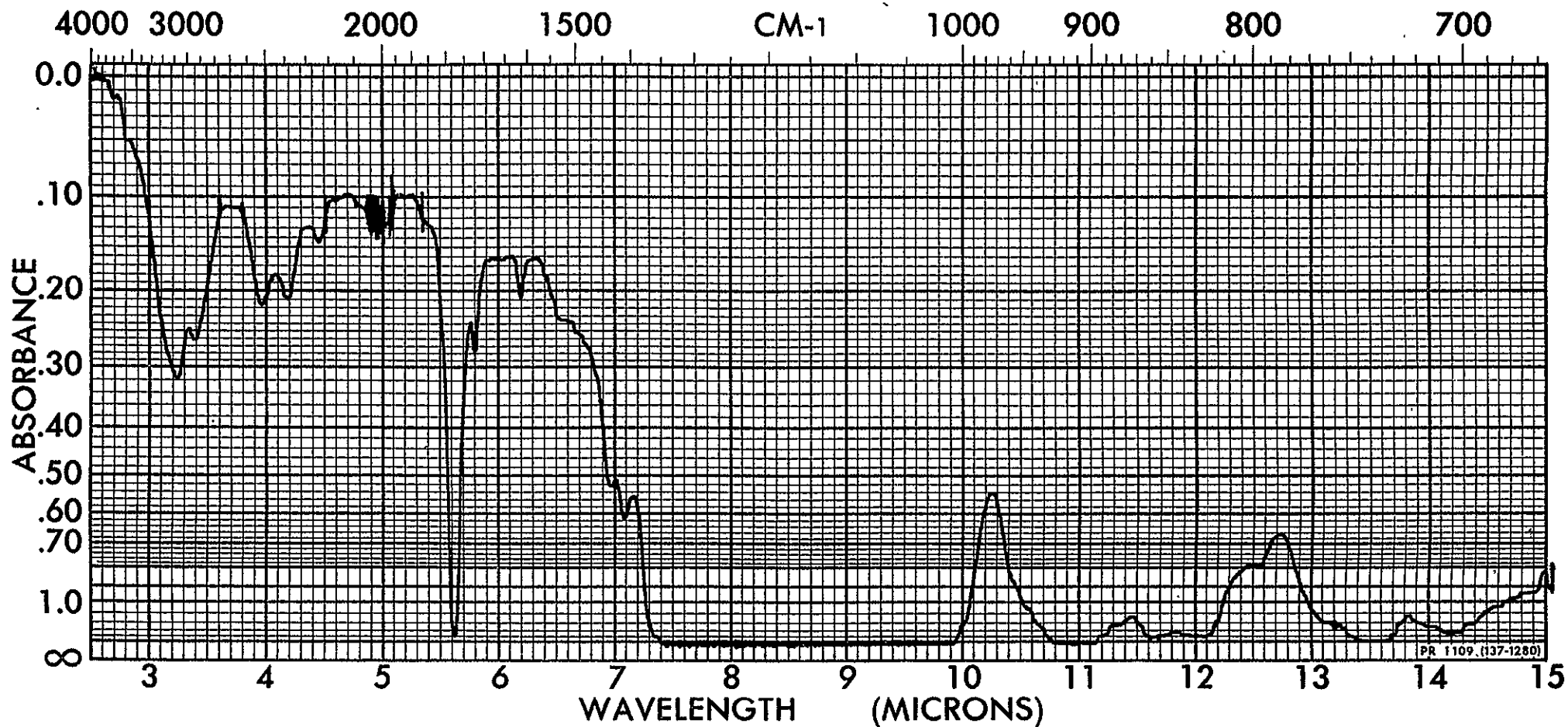
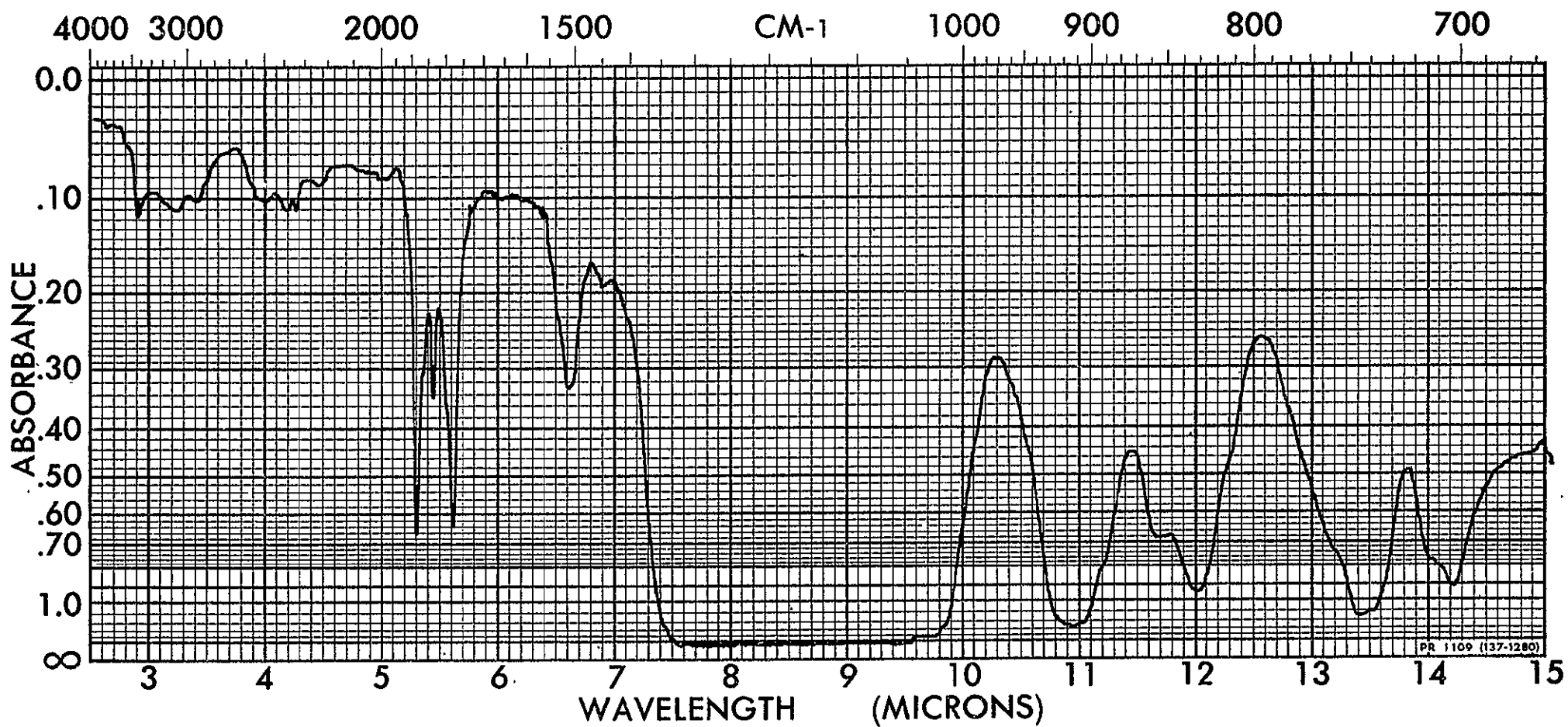Fig. 7. Infrared Spectrum: Polymer Run No. 13 - Unsaturated Carboxylic Nitrosofluorocarbon

Fig. 8. Infrared Spectrum: Polymer Run No. 13 - Ozonolysis Product of Unsaturated Carboxylic Nitrosofluorocarbon
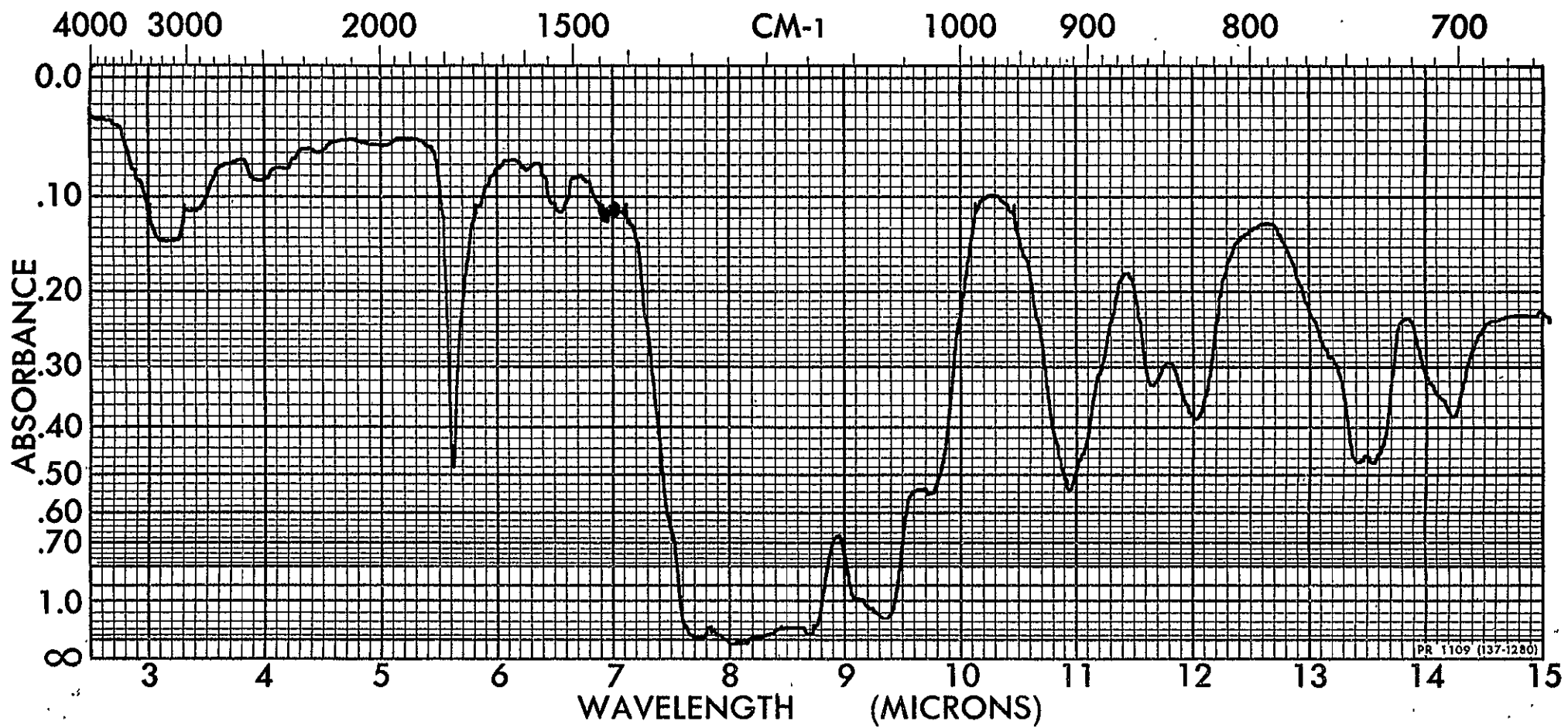
Fig. 9. Infrared Spectrum: Polymer Run No. 13 - Carboxylic Nitrosofluorocarbon

oxidation of unsaturated terpolymers. The cures are described below for the various polymers. Thus:

(a) Polymer No. 13 Products

1) ERLC-4207; 1 equivalent of curative gave a clear liquid which thickened gradually over 1 hr. Cure at 180°F gave a transparent, tack-free disk.

2) ERLA-4221; 1 equivalent of curative gave an immediate reaction and rapid cure. 180°F treatment gave a transparent, tack-free disk.

(b) Polymer No. 16 Products

1) ERLC-4207; 1 equivalent of curative gave a clear liquid which thickened in 45 minutes with considerable entrapment of air. Cured at 180°F to give a disk that was very crumbly due to entrapped bubbles of air. Bubbles obscured transparency.

(c) Polymer No. 17 Products

1) ERLC-4207; 1 gm. cup cure with equivalent of curative gave a clear liquid which thickened considerably after 45 min. Cure at 180°F gave a transparent, tack-free disk.

(3) Film Cures

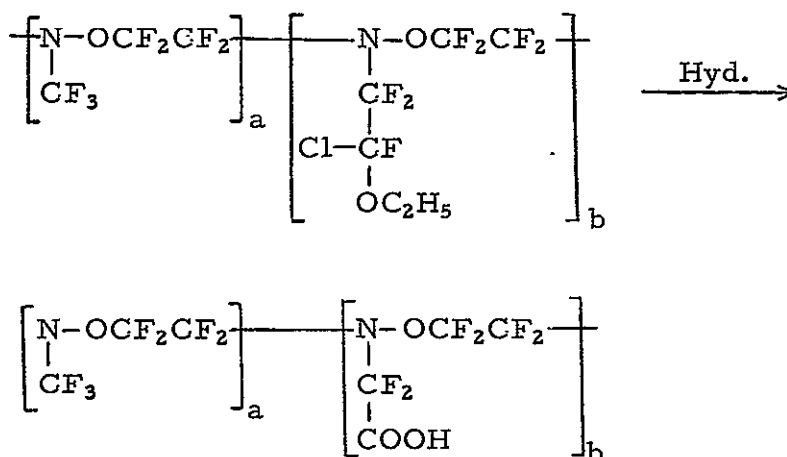(a) Polymer No. 17 Product

1) ERLC-4207; 110% of curative added to 10 g. of polymer and applied to a 3 in. x 4 in. space on a glass plate (treated with Teflon mold release agent). Cured at 180°F for 16 hrs. Film was pale yellow, easily transparent, tack-free, flexible and contained some bubbles. Film thickness ranged from 25 to 30 mils. The tensile strength ranged from 50 to 60 psi and elongation at 50%.

d. <u>Synthesis from Chlorofluoroether Polymer</u>

The employ of 2-nitroso-1-chloro-1-fluoroethyl ethyl ether (obtained by the reaction of nitrosyl chloride with trifluorovinyl ethyl ether) as a nitroso termonomer makes available a new nitroso fluorocarbon polymer containing a pendent chlorofluoro ether group. (Ref. 6) The latter group is capable of being hydrolyzed to a carboxyl group. Thus, an alternate synthesis of a liquid carboxyl containing nitroso fluorocarbon polymer is open for examination. Thus:

$$\left[\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_3 \end{array}\right]_a \left[\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_2 \\ | \\ Cl-CF \\ | \\ OC_2H_5 \end{array}\right]_b \xrightarrow{\text{Hyd.}}$$

$$\left[\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_3 \end{array}\right]_a \left[\begin{array}{c} N-OCF_2CF_2 \\ | \\ CF_2 \\ | \\ COOH \end{array}\right]_b$$

However, efforts to hydrolyze the chlorofluoro ether group to a carboxyl by means of heating at $60\,^{\circ}C$ with water and by concentrated hydrochloric acid were not successful.

The success of the chlorine-Freon 113 modified terpolymerization program reported earlier had minimized the need for any further work on this approach.

2. <u>Hydroxyl Functioned Nitrosofluorocarbon Polymer</u>

a. <u>Ethylene Oxide-Liquid CNR Product</u>

The hydroxyl group present in the hydroxyethyl ester of a nitrosofluorocarbon furnishes a site for a cure reaction with the use of a diisocyanate. The hydroxyethyl ester may be depicted via the reaction of ethylene oxide with a carboxy nitrosofluorocarbon. Thus:

$$\text{Polymer}\left\{\begin{array}{c}\text{N}-\text{OCF}_2\text{CF}_2\\ |\\ \text{C}_3\text{F}_6\\ |\\ \text{COOH}\end{array}\right\}_n + \begin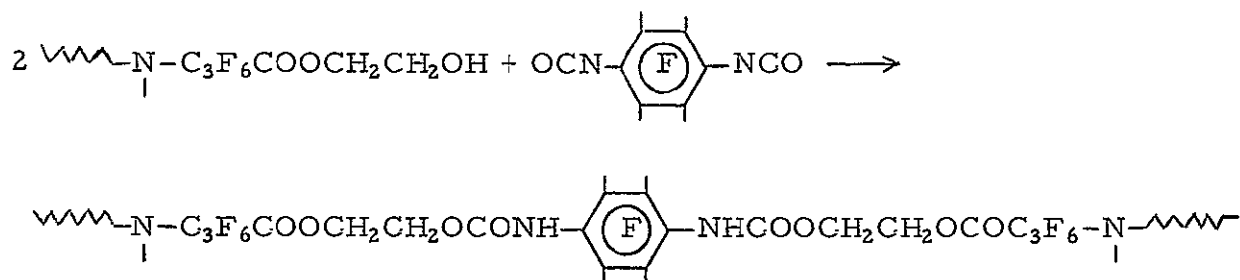{array}{c}\text{CH}_2-\text{CH}_2\\ \diagdown\ \diagup\\ \text{O}\end{array} \longrightarrow \text{Polymer}\left\{\begin{array}{c}\text{N}-\text{OCF}_2\text{CF}_2\\ |\\ \text{C}_3\text{F}_6\\ |\\ \text{COOCH}_2\text{CH}_2\text{OH}\end{array}\right\}_n \cdot$$
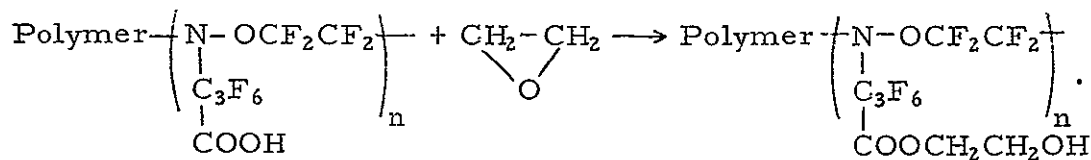
    The cure reaction of the adduct with a diisocyanate is represented thus to give a urethane linking group.

$$2\ \sim\!\!\!\sim\!\!\!\sim\!-\text{N}-\text{C}_3\text{F}_6\text{COOCH}_2\text{CH}_2\text{OH} + \text{OCN}-\langle\!\langle\text{F}\rangle\!\rangle-\text{NCO} \longrightarrow$$

$$\sim\!\!\!\sim\!\!\!\sim\!-\text{N}-\text{C}_3\text{F}_6\text{COOCH}_2\text{CH}_2\text{OCONH}-\langle\!\langle\text{F}\rangle\!\rangle-\text{NHCOOCH}_2\text{CH}_2\text{OCOC}_3\text{F}_6-\text{N}-\sim\!\!\!\sim\!\!\!\sim$$

    The available diisocyanate of current interest is the Whittaker Corporation's 6-chloro-2,4,5-trifluoro-1,3-phenylene diisocyanate. The choice of a fluorinated aromatic diisocyanate was made to improve miscibility with the fluorocarbon polymer and to introduce a minimal amount of hydrogen.

    An earlier Thiokol program had established that carboxyl containing nitrosofluorocarbons were capable of reacting with ethylene oxide to form the 2-hydroxyethyl ester. This conclusion was based on the change in the infrared spectrum of the reaction product from the starting material. The present work sought to establish more completely the nature of the ethylene oxide adduct and to determine its efficacy in a cure reaction with a fluorinated diisocyanate.

(1) Preparative Procedure

    The carboxy material used was the liquid polymer from Polymerization Run No. 23, a terpolymer of tetrafluoroethylene, trifluoronitrosomethane and 7.5 mole % perfluoronitrosobutyric acid, prepared in Freon 113 solvent and modified by 2.5 mole % chlorine. The viscosity was 262 poises. The carboxyl titre was .60 meq/gm. The specific gravity was 1.87.

The reaction with ethylene oxide was carried out with 450 gm. of a 33 1/3% by wt. solution of the polymer in Freon 113. The ethylene oxide was introduced at a rate of about 2 gm. per hour at $10-12°C$ with slight cooling required. The weight change in flask contents and loss of cylinder weight was followed. The introduction of 1.0 equivalent of ethylene oxide was followed by a carboxyl titre determination indicating retention of 62% of the original carboxyl. The infrared spectrum of the original material is shown in Fig. 10 while the 1:1 ethylene oxide adduct is shown in Fig. 11. The presence of considerable carboxyl is evident in Fig. 11 by the broad absorption at 2.8 to 4.0μ. Additional amounts of ethylene oxide were introduced and the data reflecting change in carboxyl titre is shown below:

Equivalents of E.O. Added	% Carboxyl Remaining
1.0	62
2.0	45
3.0	15
4.0	13

The infrared spectrum of the 4:1 adduct is shown in Fig. 12, exhibiting absorption at 2.95μ for the hydroxyl and 3.45μ for C-H. The spectrum is in essential agreement with that obtained in the earlier RMD-Thiokol 5126 program on Conformal Coatings.

It thus appears that the product of the reaction of ethylene oxide with a carboxy nitrosofluorocarbon is not the simple 2-hydroxyethyl ester but rather a polyethyleneglycol ester. In the above instance the following representation may be made:

$$\text{wwwN-}C_3F_6\text{-COOH} + 4\ CH_2\!\!\diagdown_{\!\!O}\!\!\diagup CH_2 \longrightarrow \text{wwwN-}C_3F_6COO(CH_2CH_2O)_4H$$
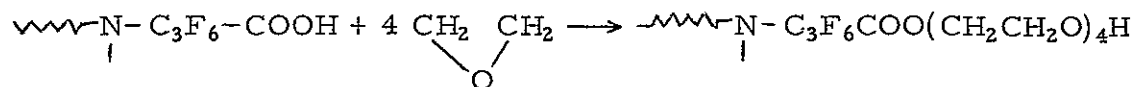
The product obtained thereby contains 10% of its weight as derived from ethylene oxide. The impact of the added hydrocarbon content on the flammability of a cured product is examined in the section on film evaluation and testing.
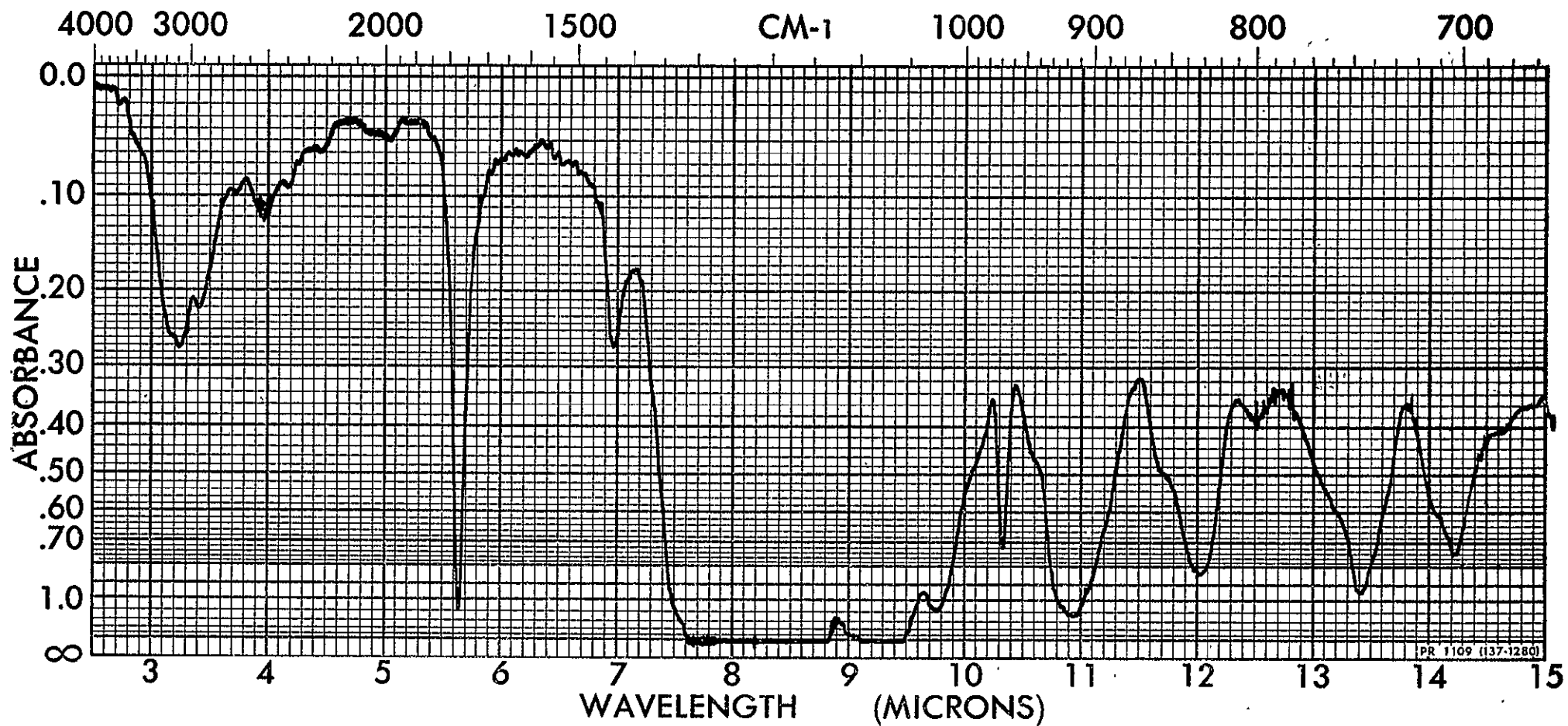
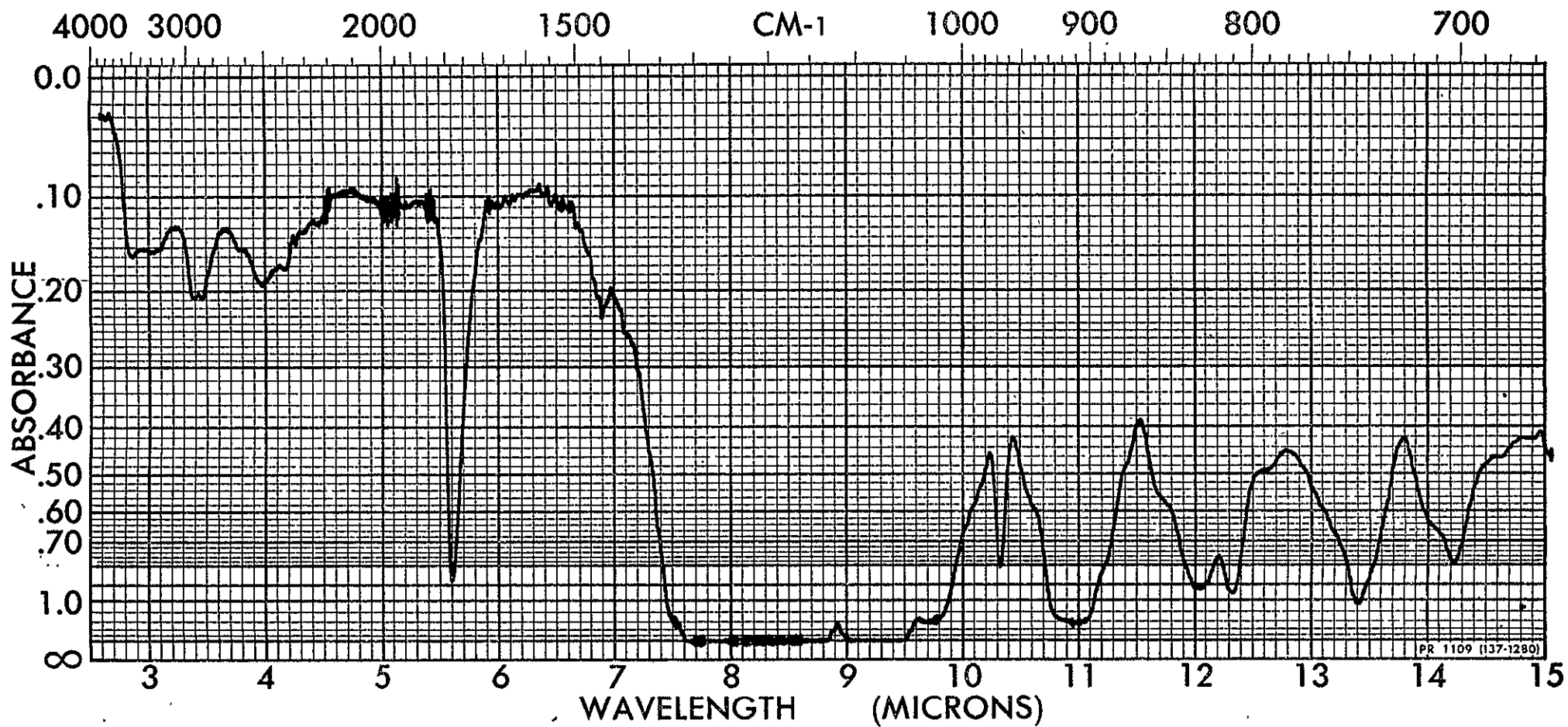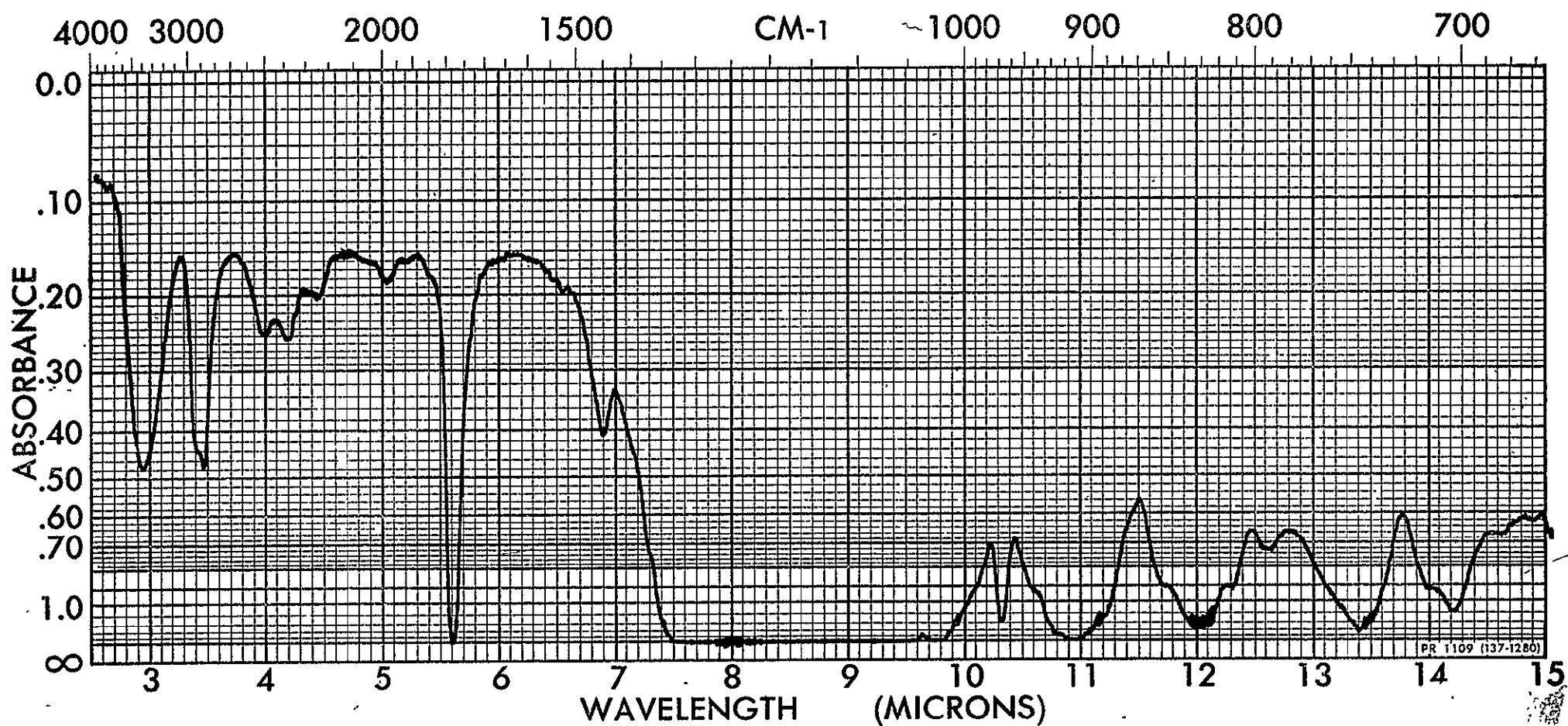Figure 1,0. Infrared Spectrum - Carboxy Nitrosofluorocarbon - Run No. 23

Figure 11. Infrared Spectrum - 1:1 Ethylene Oxide:Carboxy Nitrosofluorocarbon - Run No. 23

Figure 12. Infrared Spectrum - 4:1 Ethylene Oxide:Carboxy Nitrosofluorocarbon - Run No. 23
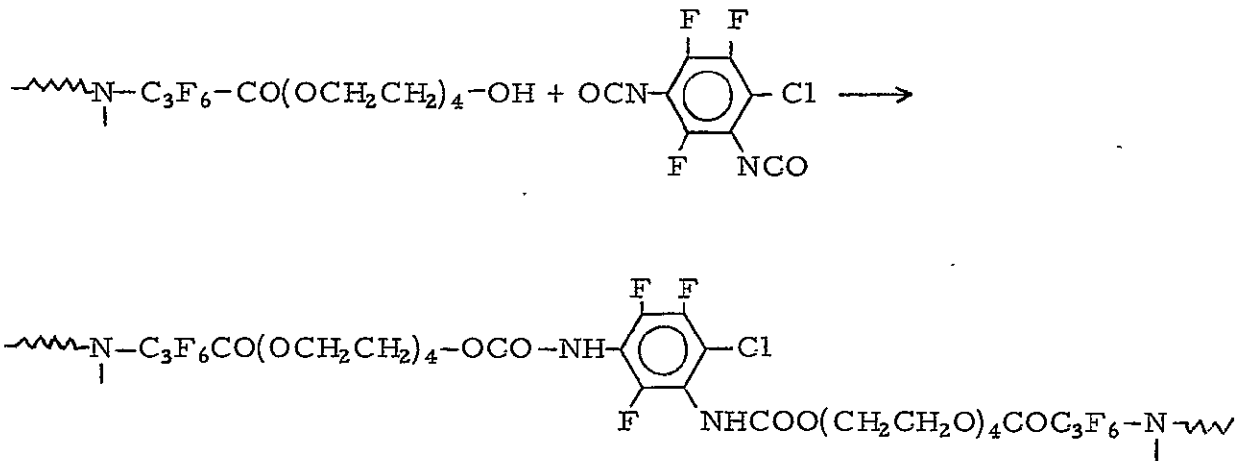
The viscosity of the ethylene oxide adduct was 117 poises. The active hydrogen content was calculated at .54 m. e. q. /gm. for purposes of a cure reaction. The product was noted as the ethylene oxide adduct of Polymer Run No. 23.

The product had a specific gravity of 1.85.

(2) Cup Cure

The product prepared by the reaction of ethylene oxide and liquid CNR is an hydroxyethyleneoxy ester of a carboxy nitrosofluorocarbon polymer. The reaction of the hydroxyl group with 6-chloro-2, 4, 5-trifluoro-1, 3-phenylene diisocyanate is capable of providing a urethane linking group. Thus:

$$\text{-----N-C}_3\text{F}_6\text{-CO(OCH}_2\text{CH}_2)_4\text{-OH} + \text{OCN-} \underset{\underset{\text{F}}{\overset{\text{F}\quad\text{F}}{}}}{\boxed{\bigcirc}} \overset{}{\underset{\text{NCO}}{}}\text{-Cl} \longrightarrow$$

$$\text{------N-C}_3\text{F}_6\text{CO(OCH}_2\text{CH}_2)_4\text{-OCO-NH-} \underset{\underset{\text{F}}{\overset{\text{F}\quad\text{F}}{}}}{\boxed{\bigcirc}} \overset{}{\underset{\text{NHCOO(CH}_2\text{CH}_2\text{O})_4\text{COC}_3\text{F}_6\text{-N}}{}}\text{-Cl}$$

A cup cure was examined with 2 gm. of 4:1 ethylene oxide adduct of Polymer Run No. 23 and .15 gm. of 6-chloro-2, 4, 5-trifluoro-1, 3-phenylene diisocyanate. A homogeneous mix was readily obtained which thickened after 5 minutes. Standing at ambient temperature for 1 1/4 hours gave an almost complete cured disk of low tack with some bubbling. Cure at 180°F for 16 hours gave a bubbled disk of no tack.

Since the starting material contained 13% of its active hydrogen as carboxyl the formation of bubbles may be due to carbon dioxide liberation.

(3) Cured Film and Evaluation

(a) Film Deposition and Adhesion

A 2 gm. sample of the 4:1 ethylene oxide adduct of liquid polymer No. 23 was treated with .15 gm. of 6-chloro-2, 4, 5-trifluoro-1, 3-phenylene diisocyanate. The mixture was immediately applied to a solvent-cleaned G-10 circuit board over a 1 x 3 in. area. Cured at 180°F for 16 hours. The adhesion was excellent and the film could be removed from the board by means of a razor blade.

(b) Transparency

The film obtained in (a) above had very good transparency but possessed many fine bubbles.

(c) Flammability

The film obtained in (a) above was not flammable at an oxygen pressure of 32 pounds when exposed to a glowing wire at upward propagation. However, a burning piece of paper held below the film (in an oxygen atmosphere) did result in combustion of the film. This combustion is probably the result of the impact of the added hydrocarbon content of the starting material since 10% of the product weight is derived from ethylene oxide.

(d) General Evaluation

The film from (a) above was flexible, had a fair degree of elasticity and was tack-free.

IV. CONCLUSIONS AND RECOMMENDATIONS

The CNR-Gum solvent composition prepared in this investigation shows excellent promise as a conformal coating for electronic circuitry. It has satisfied many of the requirements for such utilization. The limitations of time and scheduling did not permit a complete examination of its properties. The 25 lb. amount forwarded to the Astronautics Laboratory, Materials Division of NASA-Huntsville should permit a continued investigation of this system.

The synthesis program associated with this investigation has yielded a number of distinctive nitrosofluorocarbon materials of wide promise. The development of a diepoxide cure system has led to coatings and films of considerable merit and worth.

Liquid carboxylic nitrosofluorocarbon polymers (liquid CNR), obtained by the combined use of chlorine and Freon 113, led to a number of products having a useful viscosity and functionality range. Diepoxide cures provided coatings of excellent transparency, flexibility, adhesion and complete cure characteristics. This development is worthy of further study to afford a more complete examination of its utility. A large variety of these products were submitted to the Astronautics Laboratory, Materials Division of NASA-Huntsville for further use.

The preparation and ozonolysis of unsaturated carboxylic tetrapolymer has given products of promise containing both terminal and chain carboxylic functions for cure reaction. Further investigation of this approach appears warranted. The use of the intermediate acyl fluorides is also very interesting from the standpoint of preparing other functional derivatives such as alcohols, amides and amines that are susceptible to polyisocyanate cure and urethane formation.

The use of reinforcing fillers in liquid CNR-curative compositions may be worthy of examination to improve tensile strength.

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