AFML-TR-69-111, PART I

HIGH TEMPERATURE
ELECTRICAL WIRE COATINGS

Norman Bilow
Kenneth L. Rose

Hughes Aircraft Company

TECHNICAL REPORT AFML-TR-69-111, PART I

May 1969

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made ONLY with specific prior approval of the Elastomers and Coatings Branch, MANE, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

AIR FORCE MATERIALS LABORATORY
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

86

AFML-TR-69-111

HIGH TEMPERATURE
ELECTRICAL WIRE COATINGS

FOREWORD

This report was prepared by Hughes Aircraft Company, Culver City, California 90230, under Air Force Contract No. F33615-68-C-1322. The contract was initiated under Project Nr. 7340 "Nonmetallic and Composite Materials," Task Nr. 734007 "Coatings for Energy Utilization, Control and Protective Functions." The program was administered under the direction of the Elastomers and Coatings Branch, MANE, Nonmetallic Materials Division, Air Force Materials Laboratory, with Captain August H. Birke, Ph. D., serving as project engineer.

This report was submitted by the authors for publication as an AFML Technical Report in March 1969.

The principal investigator on this program was Dr. Norman Bilow, Hughes Senior Staff Chemist and Head of the Polymer and Chemical Technology Group of the Materials Technology Department. Professional assistance was received from Dr. Abraham L. Landis, Phillip Crepeau, Salomon F. Reifer and Kenneth L. Rose. Dr. L. J. Miller provided consultation on polymers and Mr. Bert Gerpheide provided consultation on electrical wire properties. Wire insulation was wrapped at the Microdot Corporation under the supervision of Mr. Richard Holzhauer.

This report covers work conducted between February 1, 1968 and February 1, 1969 and is the first interim annual report on this two year contract.

This technical report has been reviewed and is approved.

WARREN P. JOHNSON, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The purpose of this research was to develop new and improved polymeric coatings for electrical wire which are stable to temperatures above 500°F (up to 800°F) for use on future high speed (greater than Mach 3) aircraft and missile systems.

Polyimidazopyrrolone ("Pyrrone"), perfluoroalkylenetriazine, silicone carborane, bisbenzimidazolebenzophenanthroline (BBB), polyphenylene, two polyimides, polyphenylsilane, carborane modified polybenzimidazole, and polyxylylene were investigated as potential high temperature polymeric wire coating materials. "Pyrrone" and the two polyimides were found to be excellent adhesives for Kapton polyimide film, whereas the silicone carborane and perfluoroalkylenetriazine showed poor adhesion for Kapton. Polyphenylene (Abchar 412) also showed excellent adhesion for Kapton but lost this adhesion under high temperature thermal aging.

"Pyrrone," perfluoroalkylenetriazine and silicone carborane all had very good dielectric properties. "Pyrrone" has been successfully used as a Kapton sealant and wires containing this combination have survived 28 day humidity tests at 95 percent RH at 185°C without peeling. Such wires had poorer dielectic properties when wet, but regained their properties when redried. Dielectric properties of the "Pyrrone"-Kapton combination depended upon the cure process used; however, a good reproducible cure cycle has been developed.

A new cure process for perfluoroalkylenetriazine elastomer was discovered which functions at ambient temperature or higher. Cures were achieved in 2 days at 25°C, in 2 to 3 hours at 50 to 60°C or almost instantly at 150°C. The curing agent is terephthalonitrile-N,N'-dioxide and is effective in concentrations of 1/4 to 2-1/2 percent. Elastomer cured by this curing agent is far more resistant to moisture than the tetraphenyltin cured elastomer. Investigation of the triazine polymer cured by this improved process is continuing.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made ONLY with specific prior approval of the Elastomers and Coatings Branch, MANE, Nonmetallic Materials Division, Air Force Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Table | Page

I. INTRODUCTION

The evolution of aircraft operating at speeds in excess of Mach 3 has resulted in markedly increased temperatures to which aircraft hook-up wires are exposed. Temperatures around 550°F are commonly experienced on contemporary aircraft, while temperatures up to 800°F and possibly higher will be experienced in future hypersonic military aircraft. These temperatures are considerably in excess of those that existing aircraft hook-up wires can safely withstand under sustained conditions.

The high temperature hook-up wire currently specified for military aircraft has a thin (3-mil maximum), tough insulation and is procured against specification MIL-W-81381, "Wire, Electric, Polyimide Insulated, Copper and Copper Alloy." The insulation on this wire is constructed from tapes that are composites of polyimide and FEP fluorocarbon polymer. This wire has a continuous service temperature rating of only 392°F. When it is subjected to temperatures slightly above 400°F, the FEP fluorocarbon sealant exceeds its yield strength. As a result the insulation loses its sealant properties, and a general reduction in mechanical properties is observed. Thus to improve the thermal threshold of hook-up wire, it would be necessary to utilize a sealant that could be substituted for the FEP layer of the wire insulation and that has a service temperature equal to or better than that of the polyimide film alone.

Many high temperature polymers that warranted evaluation as sealants in this program have been under development at laboratories throughout the country. Polyimides, silicone carborane (Dexsil*) elastomers, polyphenylenes, perfluoroalkylenetriazines, "Pyrrones," BBB resins, polybenzothiazole, poly(terphenylene oxide) and PBI-quinazoline were selected as primary candidate sealants because of the high probability that they would meet the high temperature insulation requirements. Furthermore, several of these polymers were

---

*Olin Mathieson Chemical Corp. trade name.

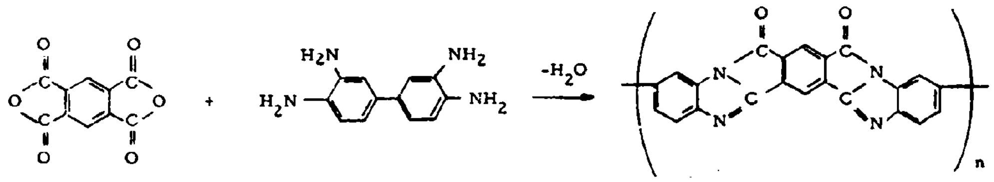
available in research quantities and consequently their evaluation was feasible within the scope of this program. Other rarer prospective polymers also exist and warrant screening in subsequent investigations.

II. POLYMERIC WIRE COATINGS DEVELOPMENT

A. "PYRRONE"

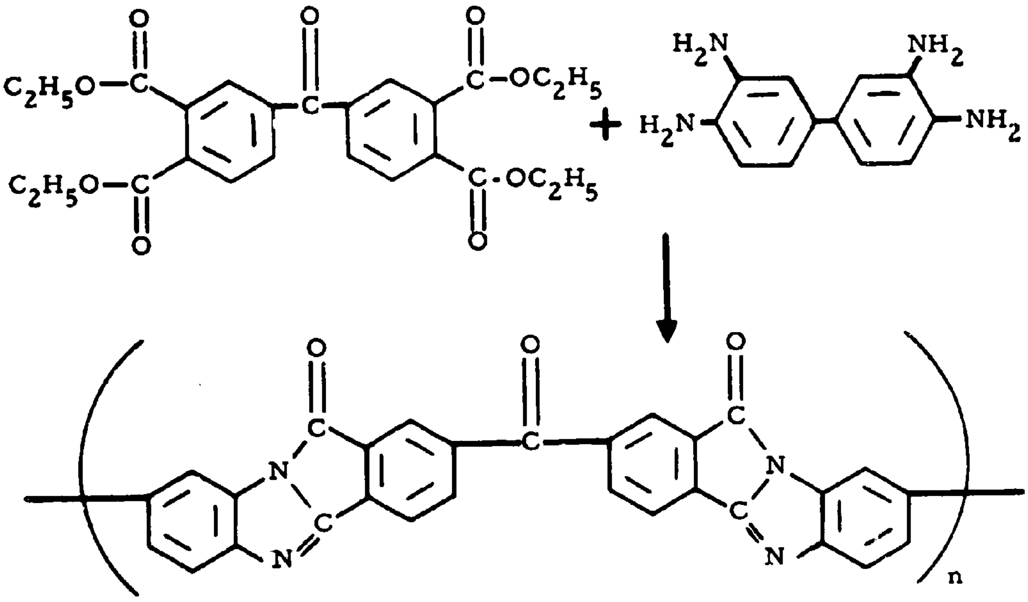
"Pyrrone" resins are condensation polymers derived from aromatic dianhydrides and tetraamino aromatic compounds. Bell and Pezdirtz[1] originally referred to these polymers as polyimidazopyrrolones, whereas Colson, Michel, and Paufler[2] described them as polybenzoylenebenzimidazoles. Dawans and Marvel[3] have also investigated these polymers but used no general terminology to name them.

Typically, the "Pyrrone" resins are derived from a dianhydride such as pyromellitic dianhydride or benzophenonetetracarboxylic dianhydride, and a tetraamine such as 1, 2, 4, 5-tetraaminobenzene, 3, 3'-diaminobenzidine, or 3, 3', 4, 4'-tetraaminodiphenyl ether. A typical polymerization is illustrated below:



"Pyrrone" polymers prepared from aromatic dianhydrides are infusible and completely intractable materials, and consequently they have found no application as molding materials, laminating resins, extrusion compounds, etc.

Subsequent to the work of Bell and Pezdirtz; Colson, Michel and Paufler; and Dawans and Marvel, the Hughes Aircraft Company, under NASA contract NAS 1-6287 studied methods of processing the "Pyrrones." In the course of this study, the condensation of tetraethyl benzophenonetetracarboxylate and 3, 3'-diaminobenzidine was investigated. The reaction is illustrated below:



The polymer structure illustrated is theoretical. In actual practice, it is evident that other functional groups are also formed. Thus, the cured polymer probably contains benzimidazole moieties, imide groups and even some amide groups, and consequently, the term "Pyrrone," as originally used by Pezdirtz and Bell, is not really appropriate terminology. Benzimidazole groups can be expected to form via the loss of CO_2 from the carboxyl substituted imide intermediate when the cure is conducted above 250°C.

Evidence for the variation in composition at the different cure temperatures is obtained from elemental analyses. For example, the following analytical data was collected on polymer cured at 300°C (572°F) and 350°C (662°F).

	Percent C	Percent H	Percent N	Percent O
at 300°C	73.69	3.49	11.32	10.69
at 350°C	74.91	4.12	11.59	9.24
calc. for $C_{29}H_{12}O_3N_4$	75.00	2.60	12.06	10.33

The benzophenonetetracarboxylic acid tetraethyl ester based polymer has shown excellent thermal stability, and has a major advantage over other "Pyrrone" resins in that it is easily processed. The prepolymer is readily soluble in dioxane and chloroform. It is also thermosetting. Consequently, polymer "lacquers" or "varnishes" can be prepared from the prepolymer which can be applied to substrates by spraying, brushing, or dipping, and can be dried and cured subsequently to provide useful composite structures. For these reasons, this specific "Pyrrone" was rated as an important candidate electrical wire insulation.

The first approach to utilizing "Pyrrone" resin was to evaluate the polymer as an adhesive for Kapton* polyimide film. Chloroform solutions of the "Pyrrone" prepolymer (0.33 g./cc) were sprayed onto 6 inch by 12 inch by 5 mil Kapton and 2-ply laminates were subsequently formed and press cured at 100 psig. T-peel samples 1 inch by 12 inches were then cut from the larger sheets and were tested on the Instron Universal Testing Instrument using standard ASTM procedures. The jaw separation rate was set at 10 inches per minute. Measurements at 800°F were carried out by heating the specimens between two banks of 30 kw quartz lamps. Such heat lamps were preferred to the environmental chamber for these tests because test temperatures could be reached almost instantly with them, whereas with the chamber a significant warm-up time was required each time a new specimen was inserted,

---

*E.I.duPont deNemours & Co. trade name.

since the chamber cooled significantly when opened for sample change. Three thermocouples mounted near the specimens were used to monitor temperatures in three positions simultaneously. Photographs of two typical tests are shown in Figure 1.

a. Before Test-During Heatup b. During Peel Test at 800°F and 600°F

Figure 1. Typical High Temperature Tensile Peel Tests Using the 30 KW Quartz Heat Lamps

Samples tested at ambient temperature (75°F, 24°C), without thermal aging, or with thermal aging for 2 hours at 600°F (316°C) or 2 hours at 800°F (426°C), failed in the Kapton substrate rather than peeling. Similar results were observed in 800°F tests on unaged samples as well as thermally aged (2 hours at 600°F or 2 hours at 800°F) specimens. Samples were tested in triplicate and in only two series of samples was peel observed in one of the set of three. In both cases these were samples which received the 2 hours heat soak at 800°F. From the results of these tests, it was quite apparent that "Pyrrone" resin bonded very well to Kapton polyimide film and consequently its other electrical and physical properties also warranted evaluation.

"Pyrrone" prepolymer cures via the elimination of both ethanol and water. Consequently, considerable care is required to produce laminates with void-free interlayers. This problem is, of course, also observed with the polyimide adhesives described elsewhere in this report, although the problem appears to be less serious with the "Pyrrone."

To take advantage of its thermosetting character, efforts subsequently were made to determine the degree to which the resin had to be "advanced" prior to bonding the "Pyrrone" coated Kapton substrates. As the "Pyrrone" resin is "advanced," the volatile byproducts are evolved; therefore, the further the resin advances prior to sealing, the greater is the probability of producing continuous void-free interlayers. However, as the degree of polymerization increases the required molding pressures and/or temperatures increase. Since the "Pyrrone" resin is to function as a sealant for wire wrapped insulation, relatively low wrapping pressures would have to be utilized and thus relatively low molecular weight prepolymers would be required for processing.

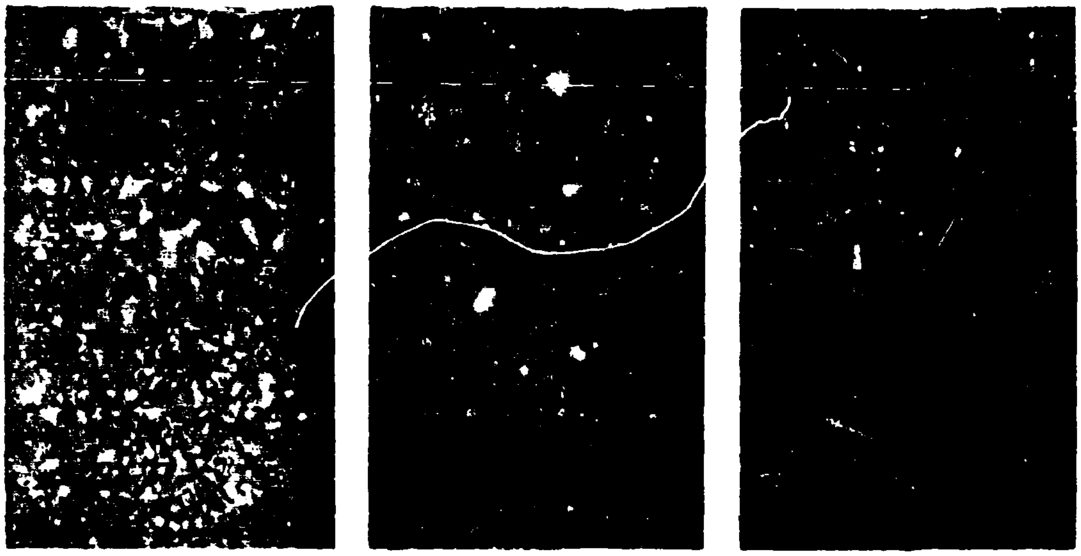
After the preliminary screening tests were completed, a series of "Pyrrone" coated Kapton specimens were prepared and subsequently B-staged in nitrogen at 200°C for (1) 15 minutes, (2) 30 minutes, (3) 45 minutes, (4) 60 minutes, and (5) 120 minutes. Each of these coated films was then cut into 3 inch by 6 inch samples which were bonded together and cured at 200°C under pressure using the conditions shown in Table I.

From the results of these tests, it was apparent that the "Pyrrone" resin did not seal well at 200°C (392°F) if it was B-staged longer than 45 minutes. It was necessary, therefore, to reexamine the sealing characteristics at significantly higher temperatures and efforts thus were subsequently made to bond specimens at 250°C (482°F) and 300°C (572°F) using a prepolymer which was B-staged for 1 to 1-1/2 hours.

Figure 2 shows photographs of three typical "Pyrrone" bonded Kapton laminates obtained from this series of tests. They demonstrate the relative ratio of voids in the "Pyrrone" interlayer. The

Table I. Test Conditions Used in Bonding Kapton Film Spray Coated With "Pyrrone" Prepolymer

Specimen E2259	B Stage Period, minutes	Cure		Comments	Estimated Void Content, percent
		Time, hours	Contact Pressure, psi		
$2A_1$	15	16	0.4	Good bond	
$2A_2$	15	16	1.3	Good bond	10
$2D_1$	30	16	0.4	Good bond	10
$2B_2$	30	16	1.3	Good bond	30
$2C_1$	45	64	0.4	Good bond	Bad
$2C_2$	45	16	1.3	Good bond	15
$2C_3$	45	16	4.0	Good bond	20
$2D_1$	60	64	0.4	No bond	–
$2D_2$	60	16	1.3	Poor bond	30
$2D_3$	60	16	4.0	No bond	–
$2D_4$	60	16	11.0	No bond	–
$2E_1$	120	16	4.0	No bond	–
$2E_2$	120	16	11.0	No bond	–



a. B - stage: 15 minutes Cure: 16 hours, 0.4 psi b. B - stage: 30 minutes Cure: 16 hours, 0.4 psi c. B- stage: 45 minutes Cure: 16 hours, 1.30 psi

Figure 2. "Pyrrone" Bonded Kapton Laminates

bonding conditions are specified beneath each photograph and in all illustrated cases the B - staging and cure were at 200°C (392°F).

Twenty-one T-peel tests were conducted on the series of samples described in Table I. These tests represented seven different time-temperature cure processes since they were conducted in triplicate. All samples were heated at 427°C (800°F) for 2 hours prior to testing at 800°F. In all cases the Kapton film failed at the bond line rather than failing in the adhesive. Samples varied in the amount of B-staging which the "Pyrrone" resin received as well as in the pressure used for sealing. Resin B - staged for greater than 45 minutes failed to bond at 200°C (392°F), although excellent bonds were achieved at 300°C (572°F) on samples B - staged for 60 minutes at 200°C (392°F). Cure conditions used on those specimens tested at 800°F (472°C) are shown in Table II.

Table II. Peel Tests on Various "Pyrrone" Bonded Kapton Laminates – 800° F

E2259-	Peel Strength, pounds per inch Average of Highs*	Adhesive Thickness, mils	200°C (392°F) B-Stage Period, minutes	Contact Pressure During Cure, psi
$2A_1$	0.84	0.9	15	0.4
$2A_2$	1.45	0.9	15	1.3
$2B_1$	1.37	0.8	30	0.4
$2B_2$	0.79	0.6	30	1.3
$2C_1$	1.44	0.5	45	0.4
$2C_2$	0.72	0.5	45	1.3
$2C_3$	0.84	0.7	45	4.0

*In all cases the Kapton substrate failed rather than the adhesive.

Since the thermal oxidative stability of the Kapton film appears to be the limiting factor in the "Pyrrone" bonded Kapton laminates, peel tests subsequently were conducted at lower temperatures, namely, 316°C (600°F) and 371°C (700°F).

Dielectric properties of a 1.9 inch diameter by 1/8 inch thick "Pyrrone" specimen were also determined at ambient temperature. This specimen was prepared from a polymer dried and advanced for 60 minutes at 177°C (350°F) and subsequently molded at 1000 psi for 1 hour at 260°C (500°F) followed by 1 hour at 316°C (600°F). The following results were obtained:

Dielectric constant	3.2 (at 1 kHz)
Dissipation factor	1.2 percent (at 1 kHz)
Insulation resistance (ohms)	5 x 10^{12} (at 500 vdc)
Volume resistivity (ohm cm)	2.8 x 10^{14}

Laminates B-staged for 60 to 90 minutes at 200°C (392°F) under nitrogen and thereafter cured at 300°C (572°F) for 4 hours at 100 psi were found to produce void-free adhesive interlayers. (The B-stage period varied somewhat with the resin batch.) Samples B-staged for 60 minutes at 200°C (392°F) and subsequently cured at 250°C (482°F) and 100 psi had a small percentage of voids in their adhesive interlayers, and it appeared that at this lower temperature the "Pyrrone" adhesive did not flow adequately, although good bond strength was observed.

Although satisfactory conditions were found for coating Kapton film and advancing the "Pyrrone" to a stage where it could be cured without producing interlaminar voids, it was subsequently realized that these conditions would be impractical to utilize in coating wire wrapping tapes because the tapes would have to be passed very slowly (1 hour) through an inert atmosphere oven.

To achieve more practical conditions, the "Pyrrone" prepolymer was polymerized to the point where it was on the border line of becoming insoluble in chloroform. Polymerization periods thus had to be extended for about 60 to 90 minutes. When the reaction period was extended by an additional 105 minutes, the prepolymer lost its solubility and was not suitable for use in sprayable lacquers.

Other experiments were conducted in which coated Kapton films were B-staged at 250°C (482°F) for 60 minutes and at 300°C (572°F) for 30 minutes. With either of these pretreatments, good adhesive bonds could then be obtained subsequently at 350°C (662°F).

These more advanced prepolymers were, as noted above, soluble in chloroform. However, when chloroform solutions were applied by spraying they tended to deposit in a dry particulate form rather than in the smooth film that was achieved with the less advanced prepolymer.

This was an indication of excessively rapid drying. New prepolymer lacquers then were prepared using a mixture of 80 percent chloroform and 20 percent chlorobenzene, and the coated Kapton film obtained then was dried and further advanced under nitrogen at 200°C (392°F) for 5, 10, 15, or 20 minutes. Each two-ply laminate was cured at 350°C (662°F) for 4 hours at 100 psi. These cured samples all had voids, and it was assumed that this was due to the presence of traces of residual chlorobenzene which volatilized during cure. The chlorobenzene did, of course, serve to prevent excessively rapid drying of the lacquer and thus provided uniformly coated films; however, the voids which it promoted were certainly undesirable. Subsequent experiments with a solvent mixture comprised of 95 percent chloroform and 5 percent chlorobenzene were more successful in that uniform coatings and void-free adhesive interlayers were achieved.

Three sets of void-free "Pyrrone" bonded Kapton laminates were heated at 71°C (160°F) in a 95 percent relative humidity chamber for periods of 96, 146, 157, and 264 hours. When T-peel tests were conducted on these specimens at 316°C (600°F) adhesive failure did not occur; however, those samples which received the 157 hour and 264 hour exposures did blister and delaminate. These peel tests were conducted under conditions where the temperature was raised from ambient to 316°C (600°F) in several seconds; however, in subsequent tests described later, where the exposed samples were allowed to redry adequately before testing, blistering did not occur. The blistering can, of course, be attributed to the sudden vaporization of trapped moisture. However, because such a rapid heat increase was not likely to be encountered in practice, a subsequent series of humidity tests was conducted. For this new series of tests a 3 inch by 6 inch void-free "Pyrrone" bonded Kapton laminate was prepared using "Pyrrone" resin which had been B-staged under nitrogen for 90 minutes at 200°C (392°F) after being applied to the Kapton. This specimen was cured at 100 psi and 350°C (662°F) for 4 hours and was then cut into three 1 inch by 6 inch strips. These strips were exposed to 95 percent relative humidity at 160°F for 146 hours. Specimens were then dried for: (1) 4 hours at 75°C (167°F), (2) 4 hours at 100°C (212°F), and (3) 4 hours at 150°C (302°F). Then they were placed directly into a 316°C (600°F) oven for 30 minutes. The sample dried at 150°C (302°F) did not blister, although the other two did.

These results appeared to indicate that the moisture pickup was a physical absorption since it could be reversed at 150°C (302°F), a temperature much below the cure temperature. A T-peel test was carried out at 316°C (600°F) on the redried void-free specimen, and adhesive failure did not occur. Here also the sample failed at the bond line.

Quantitative moisture absorption tests were also carried out. For these tests, 2-1/4 inch by 2 inch sheets of Kapton film (5 mil) were spray-coated on both sides with "Pyrrone" resin. The resin was subsequently B-staged under nitrogen for 90 minutes at 200°C (392°F) and then cured at 350°C (662°F) for 4 hours under argon. Samples were dried for 5 hours at 60°C (140°F) under vacuum and weighed. Uncoated specimens were used as controls.

One coated sample and one control sample then were set over water for 16 hours at ambient temperature and subsequently dried under vacuum at 120°C (248°F). In addition, one sample of each type was exposed to 95 percent relative humidity for 146 hours at 70°C (160°F), then dried under vacuum at 120°C (248°F). Weight changes which were noted under the various conditions are shown in Table III.

These tests demonstrated that the "Pyrrone" resin adsorbs water to a slightly greater extent than Kapton film. Furthermore, in the elevated temperature high humidity tests it will be noted that there was a net increase in weight (+0.70 percent) after redrying the "Pyrrone" coated substrates, whereas the uncoated Kapton showed no net water retention and actually a slight loss (-0.16 percent). Thus, it appears that in this environment Kapton adsorbs water physically, whereas the "Pyrrone" may be irreversibly absorbing water, presumably through hydrolysis. It should be noted, however, that a redried two-ply laminate which received this type of humidity test withstood peeling at 316°C (600°F) and thus adhesive failure did not occur even

Table III. Water Absorption in "Pyrrone" Coated Kapton Film

Test Conditions	"Pyrrone" Coated Kapton Percent Weight Change	Uncoated Kapton Percent Weight Change
Samples dried only	-1.68	-1.29
After ≐ 75 percent RH – 16 hours at 23°C	+1.51*	+1.30*
Redried	-0.12*	-0.06*
After 95 percent RH – 146 hours at 71°C	+3.95*	+2.19*
Redried	+0.70*	-0.16*

*Weight changes calculated on the basis of the original dried substrates.

though trace hydrolysis apparently had occurred. Furthermore, a similar sample showed no significant change in dielectric properties as a result of the humidity test. On the contrary, redried samples actually had slightly better dielectric properties in many cases.

Isothermal weight loss studies were made on "Pyrrone" prepolymer to determine the rate of polymerization on "advancement" in argon at 250°C (482°F), 300°C (572°F), and 350°C (662°F) and the results of these studies are illustrated graphically in Figure 3. It is evident from these experiments that at 250°C (482°F) the polymerization continued throughout the entire 10 hour period as shown by the continuing weight loss. In contrast, the weight loss ceased after 4 hours at 300°C (572°F) and after 3-1/2 hours at 350°C (662°F). The total weight

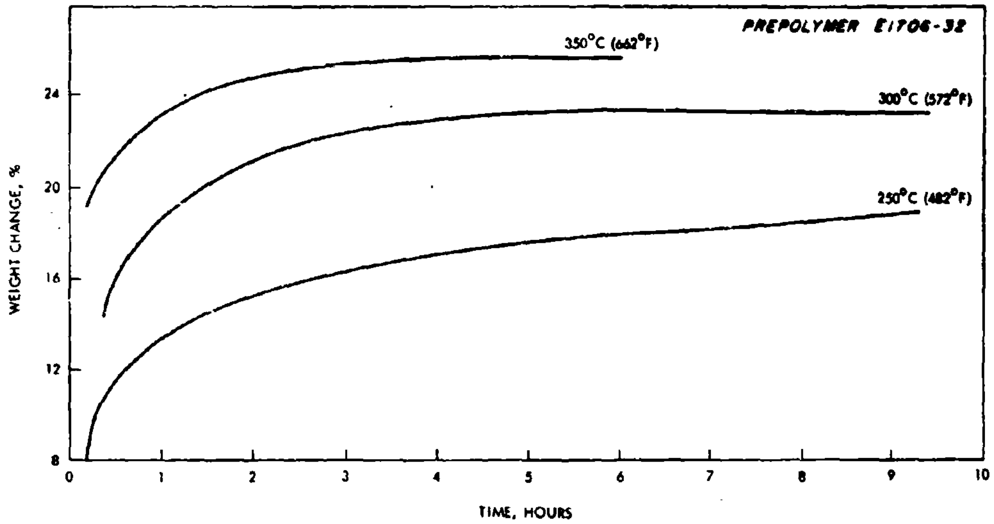


Figure 3. "Pyrrone" Prepolymer Weight Loss as a Function of Temperature

loss was different in each of these cases; thus, at 250°C (482°F) the maximum loss was 19 percent, at 300°C (572°F) the maximum loss was 23 percent and at 350°C (662°F) it was 26 percent. One may conclude from this data that the structure of the cured polymer varies to some degree with cure temperature and this would imply a variation in the ratio of the various functional groups as suggested earlier. Prepolymer used in this study had the following characteristics:

Inherent viscosity	0.46 (2.5 g/100 ml of dimethylformamide)
Equiv. percent free CO_2H	1.5

The initial polymerization conditions were: 120 ± 10 minutes at 172 ± 5°C (342°F).

Dielectric properties of a "Pyrrone" bonded Kapton laminate also were measured. The sample was one prepared from "Pyrrone" resin which had been B- staged under nitrogen for 90 minutes at 200°C (392°F) after being applied by spraying (from a chloroform solution) onto 5 mil Kapton film. Furthermore, it was cured at 350°C (662°F) for 4 hours at 100 psi and was subsequently exposed to 95 percent relative humidity at 71°C (160°F) for 146 hours, then redried for 4 hours at 150°C (302°F). Although trace hydrolysis presumably occurs during the humidity exposure, the redried laminate had excellent dielectric properties as shown below.

Dielectric constant (23°C, 1 kHz)	2.6
Dissipation factor (at 500 vdc)	0.1 percent
Volume resistivity (ohm-cm at 500 vdc)	7×10^{14}
Insulation resistance (ohm-cm at 500 vdc)	4×10^{12}

For comparison, the dielectric properties of "Pyrrone" and Kapton film alone are shown below:

	"Pyrrone"	Kapton Film
Dielectric constant	3.2	3.6
Dissipation factor	1.2	0.1 percent
Volume resistivity	3×10^{14}	10^{18} (at 125 vdc)
Insulation resistance	$>10^{13}$	–

It is quite apparent that the bonded laminate showed no significant deterioration of its dielectric properties relative to the limiting parameters of its two constituents. Its dielectric constant actually appears to be better. The bonded laminate thus withstood heat and moisture very well.

After demonstrating that "Pyrrone" was an excellent adhesive for Kapton film and that it had very good dielectric properties and water resistance, an apparatus was assembled for the continuous coating of 3/8-inch wide 3 mil thick Kapton tape with "Pyrrone" prepolymer lacquer. The tetraethyl benzophenonetetracarboxylate based "Pyrrone" resin was used for these studies also and dioxane was selected as the lacquer solvent. A schematic of this apparatus is shown in Figure 4 and a photograph is shown in Figure 5. Tape speeds varied from 2.5 to 3.5 minutes per foot, and consequently it required 5 to 7 minutes for the coated tapes to pass through the 2-foot long oven. Argon was passed through the oven continuously during this drying and B-staging period. The oven temperature varied from center to end

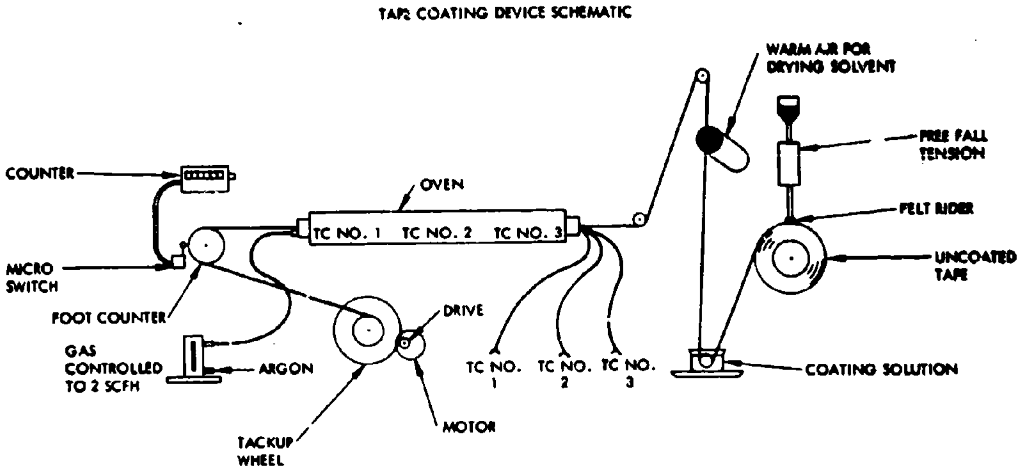


Figure 4. Tape Coating Device Schematic

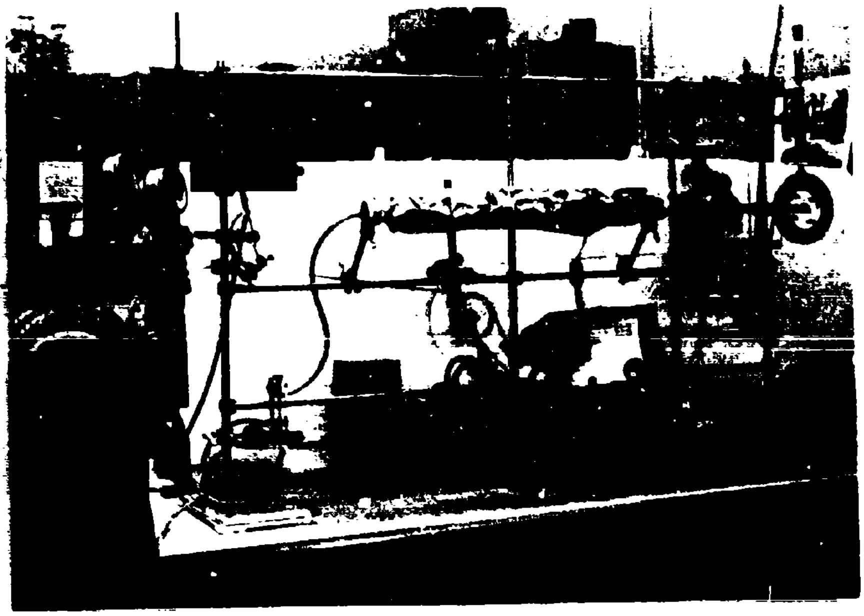


Figure 5. Tape Coating Device

and in the initial studies was 230°C (445°F) in the center while the entrance and exit temperatures were near 170°C (338°F). The argon entrance port was built into the center of the oven to provide the most uniform atmosphere distribution and minimize exposure to air. An argon gas flow rate of 2 cubic feet per hour was used.

A foot counter comprised of a micro switch and electronic countor served to determine the number of feet coated. A free falling tension device, with a felt rider, was used to provide constant tension on the roll and to control backlash. The pull force on the take-up wheel was adjusted to approximately 40 grams (which was later found to be too low).

Lacquers of various concentrations were investigated, and it was found that those containing less than approximately 28 percent resin solids provided "Pyrrone" coatings that were too thin. Solutions in the 28 percent solids content range (g/ml) provided coatings approximately 0.5 mil thick on each side of the Kapton substrate, and this was the film thickness desired. Furthermore, coatings were exceptionally uniform in appearance when they exited the B-stage oven. The "Pyrrone" was applied to the Kapton tape by drawing the tape through the lacquer and predrying with a heat gun prior to passing the coated tape through the B-stage oven.

Wire wrapping was subsequently carried out at the Microdot Corporation under subcontract to Hughes using the wrapping machine illustrated in Figure 6. Heat lamps were mounted to provide the required heat of fusion.

In preparing the first roll of "Pyrrone" coated Kapton tape the Kapton film (3/8 inch wide and 3 mils thick) was coated with "Pyrrone" prepolymer which had been advanced for 25 minutes at 200°C (392°F) under nitrogen after the resin was dissolved in dioxane to give a 28 percent solids content lacquer. Approximately 150 feet of tape then was coated and subsequently passed through a drying oven at 230°C (446°F) (center temperature). End temperatures were 150°C (302°F). The tape speed was 3 minutes per foot or 6 minutes total dwell time in the oven, and the "Pyrrone" resin was 0.5 mil thick on each side.

Figure 6. Wire Insulation Wrapping Machine

Multistrand silver coated copper wire (20 gage) was then machine wrapped with this tape. The wrapping temperature was approximately 300°C (572°F). Part of the coated wire was subsequently passed through a series of curing ovens at 260°C (500°F), 316°C (600°F), and 427°C (800°F) at a rate of 35 feet per minute (10 seconds at each temperature). It was discovered during the wrapping process that more tension was needed in the spools of tape wrapped at Hughes if uniform wraps were to be achieved.

Modifications thus were made in the Kapton tape coating device in order to provide more tightly wrapped tapes. The tension was about 30 to 40 g in this first roll and was inconsistent. Greater tension (to 200 g) was achieved by replacing the friction drive originally used with a direct drive using an 80 to 1 gear reduction connected to the motor.

Studies on possible fast post-cure conditions for the "Pyrrone" coated Kapton were next carried out to establish the feasibility of using short duration cures at temperatures of 316°C (600°F), 371°C (700°F), 427°C (800°F), and 482°C (900°F). Test conditions are shown in Table IV.

Table IV. Results of T-Peel Tests Conducted on Quick-Cured "Pyrrone"-Kapton Tapes

Sample	Cure Time minutes	Cure Temperature °F	Cure Temperature °C	Tape Speed* feet/minute	T-Peel Test Results at 700°F**
1	240	600	316	0.06	BLF
2	120	600	316	0.13	BLF
3	60	600	316	0.25	BLF
4	30	600	316	0.50	Peeled at 0.03 lb/in
5	15	600	316	1.0	No seal
6	60	700	371	0.25	BLF
7	30	700	371	0.5	BLF
8	15	700	371	1.0	BLF
9	15	800	427	1.0	BLF
10	5	800	427	3.0	BLF
11	5	900	482	3.0	BLF
12	2	900	482	7.5	BLF
13	1	900	482	15.	Peeled at 0.19 lb/in

*Calculated speed at which tape would have to be passed through the Microdot Corporation curing oven to achieve these conditions.

**BLF = bond line failure, substrate failed rather than the adhesive.

On the basis of these tests it was evident that a minimum of 60 minutes at 316°C (600°F), 15 minutes at 371°C (700°F), 5 minutes at 427°C (800°F), or 2 minutes at 482°C (900°F) was adequate for cure. However, subsequent dielectric tests on the "Pyrrone"-Kapton insulated wire showed that the 427°C (800°F) and 482°C (900°F) cures were undesirable even when the insulated wires received a postcure. These observations are discussed subsequently.

A second batch of "Pyrrone" prepolymer (E1516-97H) was "advanced" at 200°C (392°F) for 25 minutes in nitrogen, during which time its inherent viscosity increased from 0.46 to 0.56. The viscosity determination was made in dimethylformamide at a concentration of 2.5 g/100 ml. The polymer then was dissolved in dioxane (50 g/180 ml) to yield a 28 percent solids content lacquer and this was subsequently used to coat 134 feet of Kapton tape (3 mils). One hundred thirty-four feet of coated tape was prepared and B-staged for 5 minutes in argon at a temperature maximum of 280°C (536°F). This was taken up on a roll with a tension of 150 to 200 g. A second roll of tape was B-staged to a maximum of 350°C (662°F), also for 5 minutes.

The 280°C B-staged tape was wrapped on multistrand silver coated copper wire using a taping head speed of 140 rpm and a line speed of 2.5 feet to 3.5 feet per minute. The wrapping temperature was about 349°C (660°F) and the heat was directed at the location of the bend of tape around the wire inside the wrapping spindle. No crazing or uneven surfaces were produced.

The 350°C B-staged tape was wrapped using a head speed of 120 rpm and a line speed of 2.5 feet per minute. All wires were wrapped with an overlap in excess of 75 percent. Samples of this wire were inferior to the former due to a variation in tension on the tape on the roll (part of the tape had been wrapped by hand because a kink formed during the initial B-staging and necessitated rewrapping).

Sections of wire were run through the curing oven under the different conditions shown in Table V.

Table V. Cure Conditions Used in the Preparation of "Pyrrone"-Kapton Coated Wires

	B-Stage Temperature	Cure Temperature °F	Cure Temperature °C	Tape Speed, feet/minute	Total Cure Time, minutes
Wire I	Maximum 230°C	500	260	35	10 seconds
		600	316	35	10 seconds
		800	427	35	10 seconds
Wire II	Maximum 280°C				
	IIa	700	371	1	15
	IIb	800	427	3	5
	IIc	900	482	3	5
Wire III	Maximum 350°C				
	IIIa	700	371	1	15
	IIIb	800	427	3	5
	IIIc	900	428	3	5

Postcures were subsequently carried out on all of these wire samples. Wire I (E2259-32) had been wrapped with too little tension as mentioned previously. Three foot samples of the Wire I were postcured in air at 316°C (600°F) for 1/2, 1, 2, and 4 hours as well as at 371°C (700°F) for 1/2, 1, and 2 hours. All of the Wire I samples were soaked in water for 4 hours and then tested. All failed the insulation resistance test and consequently further electrical tests of Wire I were not made.

Samples of Wire II and III were also postcured as shown in Table V and subsequent dielectric test results are also shown in Table VI. These dielectric tests were made on wire soaked in water at ambient temperature for 16 to 24 hours. (MIL-W-81381 specification requires a minimum soak of only 4 hours.) Results of these tests show

Table VI. Electrical Properties of Wires Postcured in Argon Under Various Conditions

Wire Number	Test Number	Initial Cure		Post Cure		Insulation Resistance Megohms at 500 VDC	Dielectric Strength	
		Time, minutes	Temperature, °F	Time, minutes	Temperature, °F		1 Minute 2500 VAC	Maximum VAC
280°C B-Stage Wire*								
IIa	12	15	700	15	700	1.04×10^6	Passed	
	13	15	700	45	700	1.79×10^6	Passed	
	8	15	700	30	600	1.26×10^6	Passed	
	9	15	700	60	600	0.67×10^6	Passed	10.5 KV
	10	15	700	120	600	1.00×10^6	Passed	
IIb	14	5	800	15	700	2.00×10^2	Passed	
	15	5	800	45	700	62.5	Passed	
	16	5	800	30	600	1.24	Passed	10.0 KV
	17	5	800	60	600	2.28×10^6	Passed	11.0 KV
	18	5	800	120	600	2.06×10^6	Passed	
	19	5	800	240	600	2.00×10^6	Passed	
IIc	20	5	900	15	700	0.247	Passed	10.0 KV
	21	5	900	45	700	0.312	Passed	
	22	5	900	30	600	0.595	Passed	
	23	5	900	60	600	0.250	Passed	
	24	5	900	120	600	0.247	Passed	
	25	5	900	240	600	12.5		
350°C B-Stage Wire**								
IIIa	26	15	700	15	700	0.385		
	27	15	700	45	700	0.666	Passed	
	28	15	700	30	600	0.333	Passed	
	29	15	700	60	600	0.294	Passed	
	30	15	700	120	600	0.830	Passed	11.0 KV
	31	15	700	240	600	0.666	Passed	
IIIb	32	5	800	15	700	0.67	Passed	
	33	5	800	45	700	0.36	Passed	
	37	5	800	30	600	0.21	Passed	
	36	5	800	60	600	0.11	Passed	
	35	5	800	120	600	0.096	Passed	3.5 KV
	34	5	800	240	600	0.11	Passed	
IIIc	38	5	900	15	700	0.125	50 seconds	
	39	5	900	45	700	0.167	Passed	
	40	5	900	30	600	0.146	Passed	
	41	5	900	60	600	0.111	Passed	
	42	5	900	120	600	0.143	Passed	
	43	5	900	240	600	0.167	Passed	

*Sample E2259-38A.

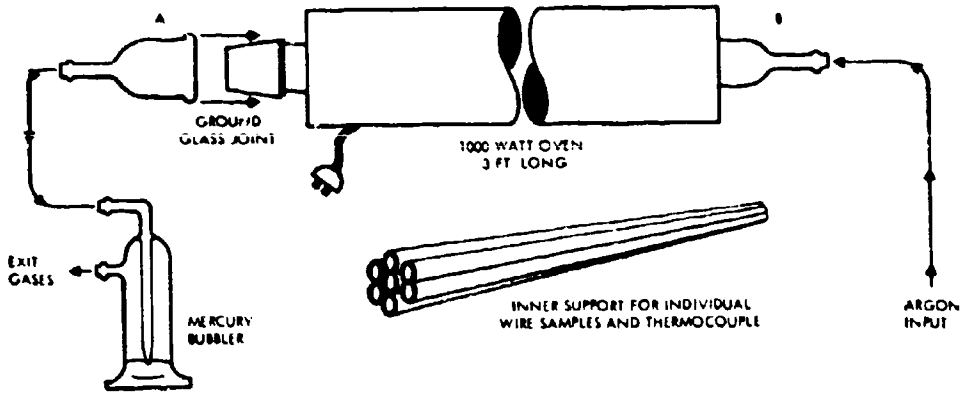
**Sample E2259-38B.

that the wire easily meets the dielectric requirements. Insulation resistance of the better wires was 1 - 2 x 10^6 Megohms (10^{12} ohms or higher) at 500 vdc and dielectric strength was 10,000 - 11,000 volts. The best wires were those B-staged up to 280°C (536°F), cured at 371°C (700°F) for 15 minutes, and postcured in argon for 4 hours at 316°C (600°F) or 371°C (700°F). Wire which was B-staged at 350°C (662°F) probably did not flow sufficiently well to seal effectively and wire cured at 482°C (900°F) probably was porous due to the excessively rapid evolution of condensation volatiles.

The insulation resistance of the cured "Pyrrone"-Kapton coated wires was determined as a function of temperature, using (1) dry wire, (2) water-soaked wire (16 hours), and (3) wire which had been exposed to 95 percent relative humidity at 85°C (185°F) for 28 days.

"Pyrrone"- Kapton insulated wires evaluated in this study were postcured under argon in the apparatus illustrated in Figure 7.

Similar tests were conducted on FEP- Kapton wire from Have Corporation. Results of these tests are illustrated graphically in Figure 8.



THE THERMOCOUPLE WAS PLACED IN THE MIDDLE TUBE OF THE INNER SUPPORT AND THE WIRE SAMPLES IN THE SIX SURROUNDING TUBES

Figure 7. Wire Post-Cure Oven

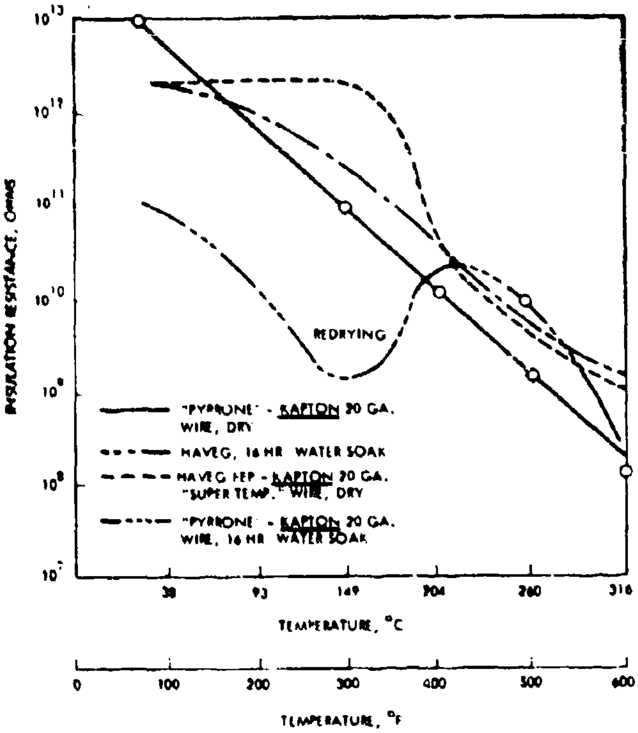


Figure 8. Effect of Temperature on Insulation Resistance of "Pyrrone"- Kapton Insulated Wire as Compared to FEP-Kapton Insulated Wire

The Haveg wire had better water resistance at ambient temperature. However, the abrupt drop in the insulation resistance of this wire from 149 to 204°C (300 - 400°F) shows that the glass transition temperature of the sealant has been exceeded and consequently the FEP sealant properties are lost. Furthermore, although its insulation resistance is slightly better than that of "Pyrrone"- Kapton wire from 204 to 316°C (400 - 600°F), adhesive failure would very deleteriously affect the physical properties of the Haveg wire. In contrast, the linear drop in insulation resistance of the "Pyrrone"- Kapton insulated wire demonstrates that the "Pyrrone" has not exceeded its glass transition temperature. This supports the previous observation that adhesive failure is not observed at 316°C (600°F) or higher. It is also important to note that the water-soaked "Pyrrone"- Kapton coated wire regains its properties when redried above 149°C (300°F) and this is also shown in Figure 8.

Humidity tests on "Pyrrone"-Kapton coated wires were carried out by exposing samples of wires to 95 percent relative humidity at 85°C (185°F) for 28 days. Tests were conducted on wire which was cured under the various conditions previously described. Although no visible change in the wires was noted, and in no case had adhesive failure occurred, there was a very significant variance in the insulation resistance depending upon the cure cycle which the wire had received. Results of these tests are shown in Table VII.

These tests indicated that the wire B-staged at 280°C (536°F), cured at 371°C (700°F) and postcured at 316°C (600°F) was significantly better than all others.

Wire samples No. 10, 19, and 24 were then retested after removing them from the aqueous surfactant solution. Tests were conducted at 24°C (75°F), 93°C (200°F), 149°C (300°F), and again at 149°C (300°F) after heating for 1 hour. Results of these tests are shown in Table VIII.

The significance of these tests can best be seen by examining Figures 9 and 10. Here the affect of redrying can be seen. Furthermore, the insulation resistance of an unexposed wire is also shown, for comparison to the redried humidity tested wire.

Efforts were subsequently made to improve the "Pyrrone"-Kapton wrapped wire by overcoating it with cured perfluoroalkylenetriazine elastomer.* To accomplish this objective, a solution of perfluoroalkylenetriazine elastomer in bis(trifluoromethyl)benzene (20 g/152 ml) was prepared. To 20 grams of this solution was added terephthalonitrile-N,N'-dioxide (0.026 g) and the mixture was stirred for 1 hour to achieve solution.

Two samples of optimally cured, post-cured "Pyrrone"-Kapton wrapped wire were then coated with the perfluoroalkylenetriazine solution and, after air drying for 2 1/2 hours, the perfluoroalkylenetriazine was cured for 2 hours at 150°C (302°F).

---

*This elastomer is discussed in detail elsewhere in this report.

Table VII. Ambient Temperature Insulation Resistance* of "Pyrrone"-Kapton Coated Wire as a Function of Cure Cycle

Sample No.	5-Minute B-Stage Temperature		Cure			Post Cure			Insulation Resistance*, ohms	
			Time	Temperature		Time	Temperature		Before Humidity Exposure	After Exposure at 95 Percent R. H. for 28 Days at 85°C
	°C	°F	Minutes	°C	°F	Hours	°C	°F		
10	280	536	15	700	371	2	316	600	1×10^{12}	7×10^{10}
19	280	536	5	800	427	4	316	600	2×10^{12}	3×10^{7}
24	280	536	5	900	482	2	316	600	2×10^{5}	2×10^{5}
31	350	662	15	700	371	4	316	600	7×10^{5}	1×10^{5}
34	350	662	5	800	427	4	316	600	1×10^{5}	1×10^{5}
43	350	662	5	900	482	4	316	600	2×10^{5}	1×10^{5}

*Tests were conducted in all cases on wire soaked in aqueous surfactant solution.

Table VIII. Insulation Resistance of "Pyrrone"-Kapton Insulated Wire After 28 Day Humidity Tests*

Temperature, °F	Sample 10	Sample 19	Sample 24
75	7×10^{11}	5×10^{11}	7×10^{10}
200	2×10^{10}	1×10^{10}	8×10^{8}
300	2×10^{10}	2×10^{10}	5×10^{9}
300 (1 hour)	1×10^{12}	8×10^{5}	6×10^{11}

*All insulation resistance values in ohms.

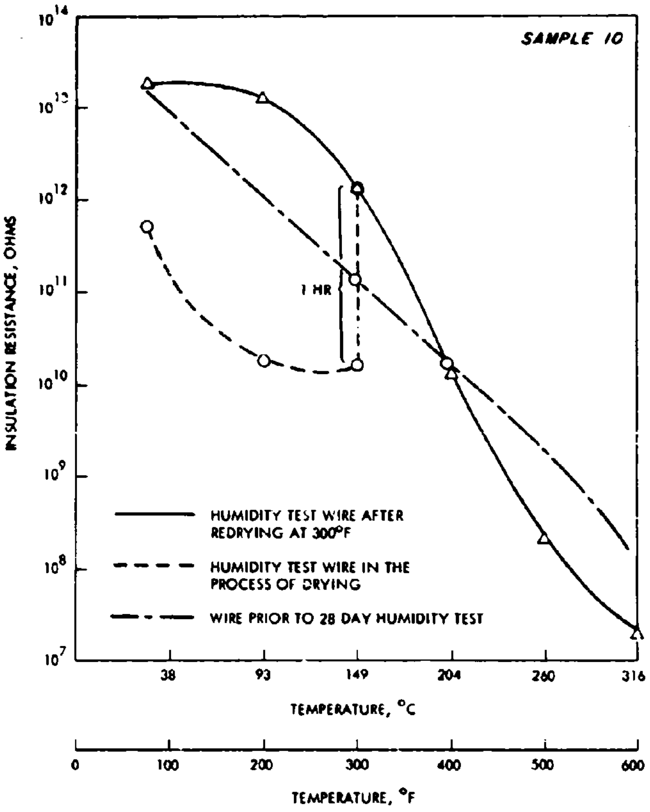


Figure 9. Insulation Resistance of Humidity Tested "Pyrrone"-Kapton Wire

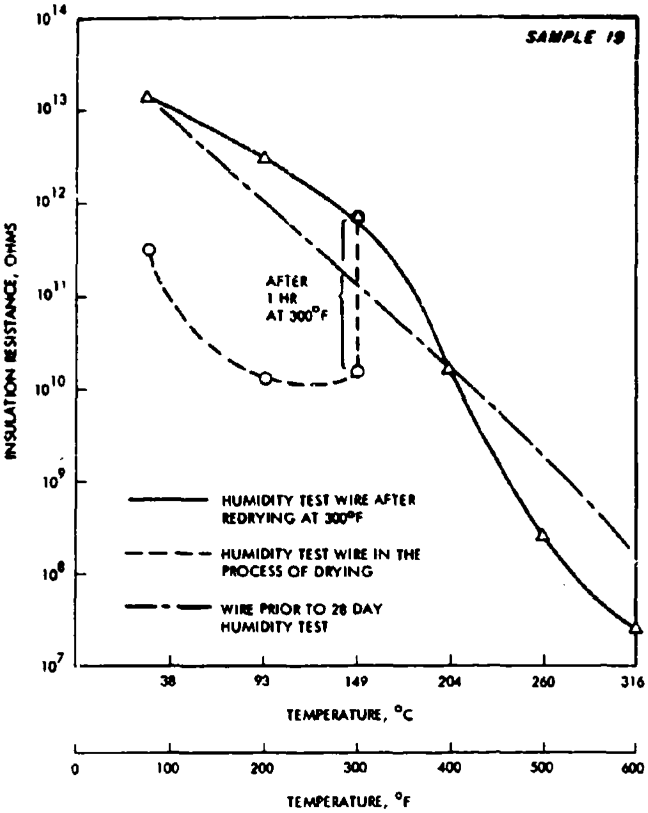


Figure 10. Insulation Resistance of Humidity Tested "Pyrrone"-Kapton Wire

One of these 3 foot long wires was soaked in aqueous surfactant solution for 16 hours. Then both wires were tested to evaluate their insulation resistance. Results of these tests are shown in Table IX. It is quite evident from these tests that the water resistance of the "Pyrrone"-Kapton insulated wire was significantly improved by the perfluoroalkylenetriazine coating. The improvement is best illustrated in Figure 11. A comparison of the overcoated dry wire with "Pyrrone"-Kapton wrapped wire is shown in Figure 12. There appears to be little advantage gained in dry tests by overcoating with perfluoroalkylenetriazine, whereas there is a significant advantage noted when one examines the aqueous surfactant soaked wires.

Table IX. Insulation Resistance of Perfluoroalkylenetriazine Coated "Pyrrone"-Kapton Wire

Temperature		Insulation Resistance, ohms	
°F	°C	Water Soaked	Dry
75	24	5×10^{12}	3×10^{12}
300	149	5×10^{11}	3×10^{12}
400	204	5×10^{10}	3×10^{10}
500	260	3×10^{9}	2×10^{9}
600	316	3×10^{8}	3×10^{8}

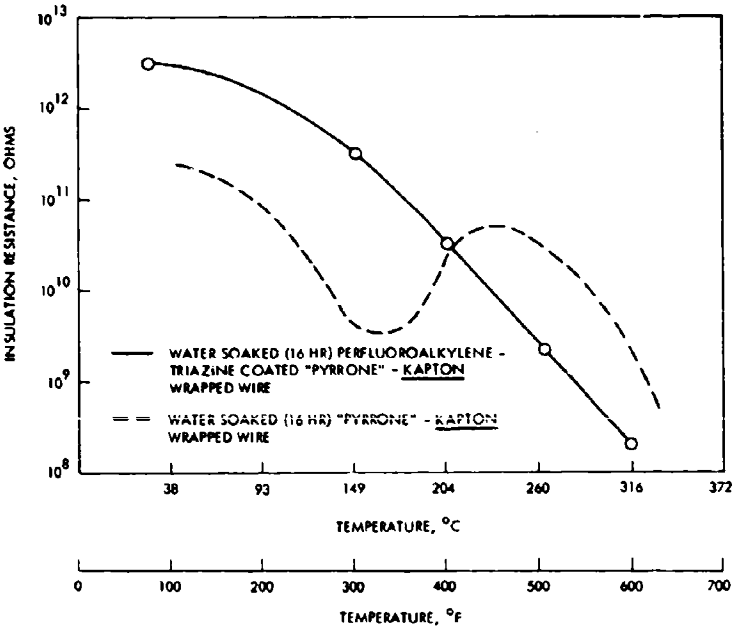


Figure 11. Insulation Resistance of Perfluoroalkylenetriazine Coated-"Pyrrone"-Kapton Wrapped Wire — Wet Tests

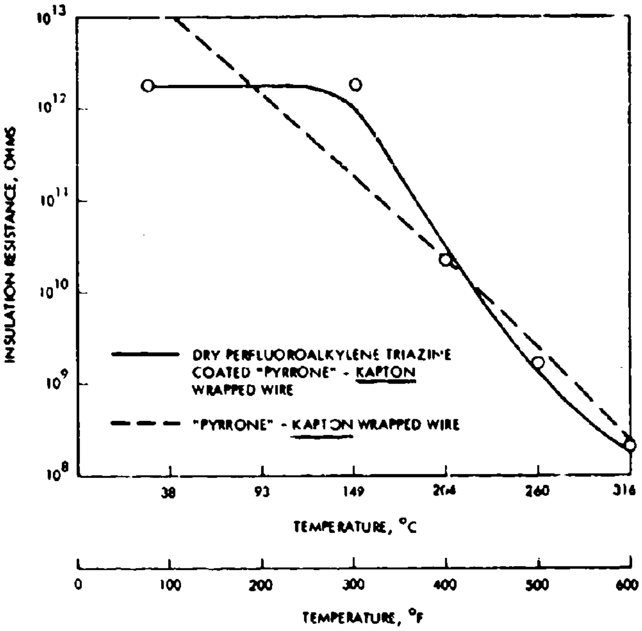


Figure 12. Insulation Resistance of Perfluoroalkylenetriazine Coated-"Pyrrone"-Kapton Wrapped Wire — Dry Tests

Synthesis of Tetraethyl Benzophenonetetracarboxylate (D1516-96)

Benzophenonetetracarboxylic acid dianhydride (193 gm, 0.6 mole) was slurried in absolute ethanol (800 ml), and concentrated sulfuric acid (28 ml) was added dropwise to the mixture. The reaction mixture then was heated to reflux and stirred for 24 hours. The crude product was concentrated by distilling off ethanol (550 ml). Benzene (400 ml) was added, and the mixture was heated to reflux for 96 hours to remove water of condensation by azeotropic distillation. Fresh ethanol was added periodically to the reaction vessel.

The final crude product, in benzene, was washed several times with fresh water, and shaken with saturated sodium bicarbonate solution to remove the partially esterified acid. The benzene solution of tetra ester then was dried over anhydrous magnesium sulfate, and the solvent was removed by vacuum distillation. The product weighed 224 grams

(79 percent of theoretical) and had 1.5 equivalent percent free carboxyl groups by analysis.

Synthesis of "Pyrrone" Prepolymer (D1516-97E)

The benzophenonetetracarboxylic acid tetra ester (141.1 gm, 0.30 mole) was heated under argon to 190°C, and solid diaminobenzidine (64.2 gm, 0.30 mole) was added to the hot stirred tetra ester. The reaction mixture was stirred under argon at 180°C for 80 minutes while the vessel was periodically evacuated to remove ethanol formed by the reaction (9.5 ml of ethanol were collected in the cold trap). The product was then cooled rapidly in an ice bath, and ground to a fine powder in a mortar. It had an inherent viscosity of 0.49 (taken in dimethylformamide solution at a concentration of 2.5 gm/100 ml).

B. PERFLUOROALKYLENETRIAZINE

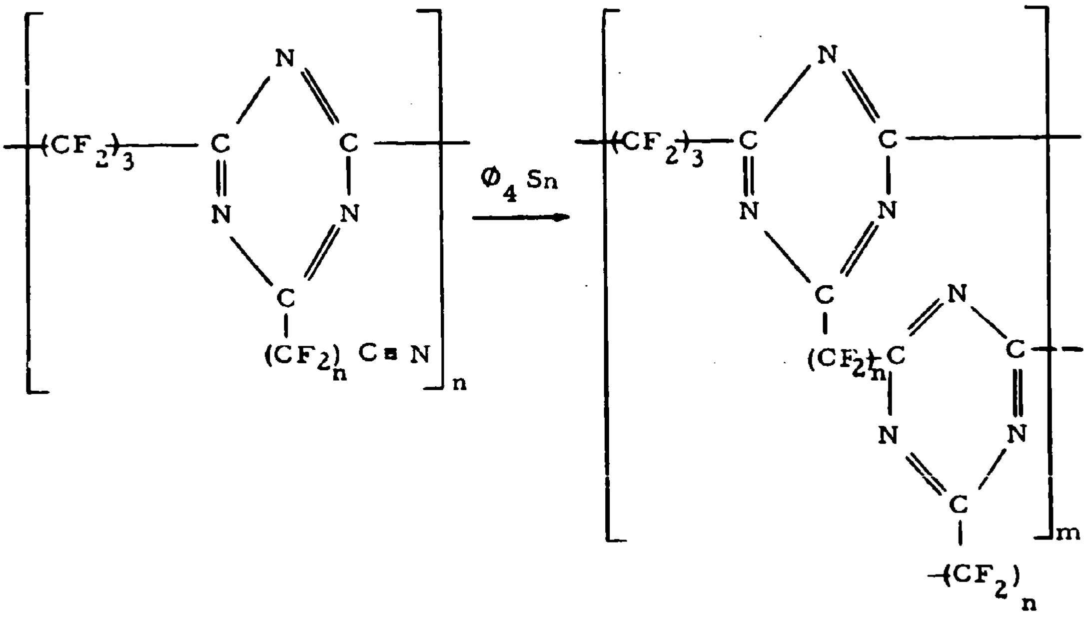
Perfluoroalkylenetriazine elastomers have been under development at Hooker Chemical Company, Dow Chemical Company, Air Force Materials Laboratory, and the University of Florida for several years. Samples of the Hooker synthesized polymer [No. 2572-17-1, prepared under AF 33 (615)-1636], were received from T. L. Graham of the AFML Elastomers and Coatings Branch for evaluation as a potential electrical wire insulation.

The elastomer is soluble in hot bis(trifluoromethyl)benzene and consequently sprayable or brushable lacquers can readily be prepared using this solvent. Extensive research also has been conducted at Hooker Chemical Company aimed at the development of an optimum cure process; as a result of that research tetraphenyltin was reported to be the best catalyst for achieving this objective. Solutions of the elastomer containing 5 percent by weight of tetraphenyltin were prepared for the wire insulation studies using the following procedure.

1. Mill the raw polymer for 5 minutes on a rubber mill.
2. Dissolve the polymer gum in m-bis(trifluoromethyl)benzene (0.2 g/ml) at 93°C (200°F).

3. Decant the solution from the insoluble polymer.
4. Add a solution of tetraphenyltin in isopropyl acetate (0.01 g/ml) sufficient to provide a 20:1 weight ratio of elastomer to curing agent.
5. Repeatedly brush coat substrates, evaporating off solvent between applications, until the desired polymer film thickness is achieved.
6. Cure the dried polymer for 24 hours at 177°C (350°F).

With tetraphenyltin as the catalyst, cure proceeds through the trimerization of pendent nitrile groups, resulting in the formation of new triazine rings as illustrated below:



This cure process was described in AFML Reports TR-64-249, Parts III and IV.

Perfluoroalkylenetriazine lacquer containing 5 percent tetraphenyltin was brush coated onto sheets of 5-mil thick Kapton polyimide film (sodium etched), and after drying, 2-ply T-peel laminates were prepared and cured as noted previously. The lacquer required heating periodically to 100°C to prevent the formation of needle-like catalyst crystals. This lacquer also was used to prepare a dielectric test specimen by brush coating a 2-inch diameter aluminum disc and repeating the process with intermittent drying until a suitable film (13.5 mil) was obtained. Ambient temperature dielectric properties of the cured perfluoroalkylenetriazine elastomer then were determined using this film with the following results.

Dielectric constant at 1 kHz	1.8
Dissipation factor	0.63 percent
Volume resistivity (ohm-cm at 500 vdc)	3×10^{12}
Insulation resistance (ohm)	1×10^{14}

These results indicate that perfluoroalkylenetriazine is an excellent dielectric material.

Kapton polyimide T-peel specimens were completely transparent and the adhesive interlayers were completely free of voids. Specimens cured for 60 hours at 177°C (350°F) had better peel strengths than those cured for 24 hours at this temperature. Higher temperature cures (24 hours at 400°F) did not appear to provide additional improvement.

Samples which were thermally aged for 4 hours at 600°F and tested at 600°F had very low bond strengths, whereas samples aged for 1 hour at 800°F and tested at 800°F were significantly better, although they could not be rated good.

Ambient temperature peel tests indicated that a cure period of 60 hours at 179°C (350°F) was significantly better than the Hooker recommended 24-hour cure at this temperature. However, it is possible that the differences observed were due to a variation in the adhesive thickness in the specimens. All specimens tested at 600°F after 4 hours of aging at this temperature had lower bond strengths than the specimens tested at ambient temperature. Samples which received the 800°F 1-hour post cure all showed "high" values of 0.58 - 0.84 pound/inch of width, although their median values were in the range of 0.18 to 0.35 pound/inch. Results of these peel tests are shown in Table X.

Table X. Results of T-Peel Tests on Perfluoroalkylenetriazine Bonded Kapton Polyimide Film

Samples D1382-	Peel Strengths Pounds/Inch of Width			Adhesive Thickness, mils	Cure Schedule		Post Cure	
	High	Low	Median		Time, hours	Temperature, °F	Time, hours	Temperature, °F
75° F Tests								
39A	0.21	0.10	0.13	0.4	24	350	–	–
39B	0.11	0.06	0.08	0.3	24	400	–	–
39C	0.86	0.49	0.67	0.2	60	350	–	–
600° F Tests								
39A	–	0.04	0.04	0.6	24	350	4	600
39B	–	0.04	0.04	0.6	24	400	4	600
39C	–	0.05	0.04	0.4	60	350	4	600
800° F Tests								
39A	0.79	0.12	0.25	0.6	24	350	1	800
39B	0.84	0.06	0.35	0.4	24	400	1	800
39C	0.58	0.07	0.18	0.5	60	350	1	800

Subsequent tests were conducted by preparing a solution of perfluoroalkylenetriazine in m-bis(trifluoromethyl)benzene and adding a solution of tetraphenyltin in ethyl acetate to provide a 5 percent by weight catalyst composition similar to that used in the lacquer described previously. Sheets of 5-mil Kapton polyimide film then were coated with these solutions, and after drying they were bonded together to provide 2-ply laminates. These laminates (6 x 3 inches) were cured under a pressure of 3.6 psi using the following cure schedules.

Specimen Number	Time, Hours	Cure Temperature		Adhesive Thickness
		°F	°C	
A_1 through A_{10}	64	350	177	0.7 ± 0.1
B_1 through B_{10}	124	350	177	0.8 ± 0.1
C_1 through C_{10}	240	350	177	0.6 ± 0.1

After cure, four samples from each of these groups were postcured at 600°F for time intervals ranging from 1/4 to 4 hours. All were found to have developed interlayers full of voids; consequently, two temperature programmed postcure schedules were established for the remaining samples. In one of these new schedules samples were sequentially postcured for 4 hour intervals at each of the following temperatures, 400°F, 450°F, 500°F, 550°F, and 600°F.

No problems were encountered at 450°F or below; however, once the specimens reached 500°F gas bubbles formed in the adhesive interlayers, and significant reductions in the interlayer thicknesses were noted. Degradation at 500°F and above obviously was occurring.

To study further methods of preventing void formation, a new series of specimens was prepared and cured at 177°C (350°F) for periods of 64, 120, 240, and 500 hours. Peel tests were then made on 1-inch wide strips of these specimens and the results are shown in Figure 13. On the basis of these tests it appears that optimum peel strengths were achieved after approximately 250 hours of cure (at 350°F) and that deterioration of the adhesive bond occurred thereafter. It is to be noted, however, that the sample that was cured for 500 hours was not prepared at the same time as the others and the possibility exists that its reduced peel strength was a reflection of an unrecognized parameter other than time.

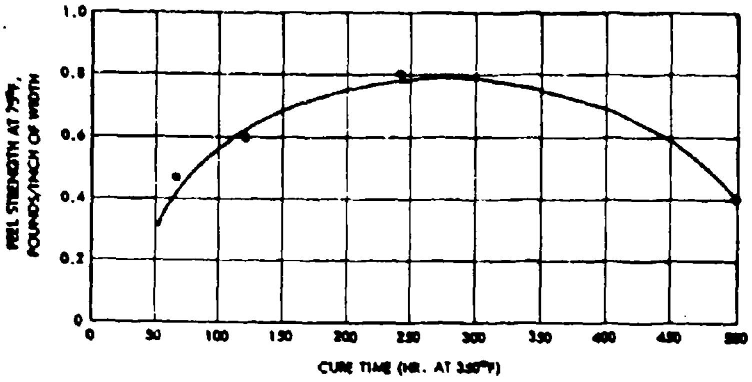
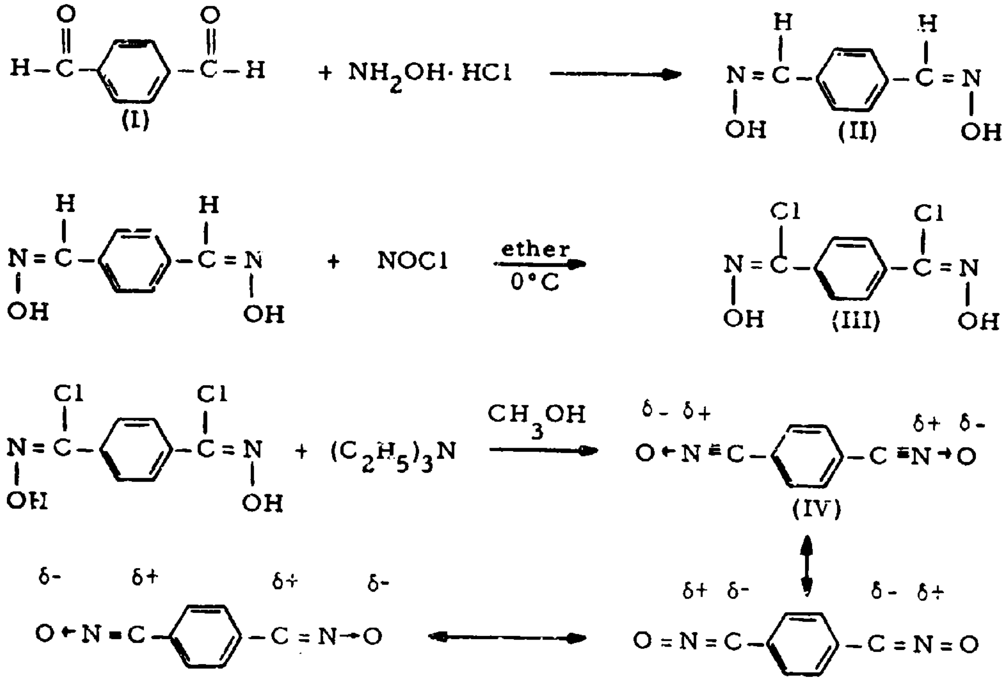
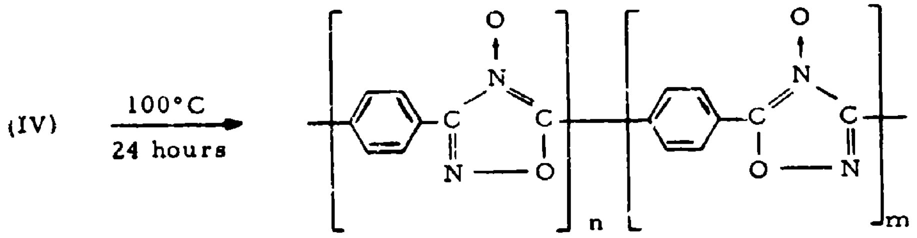


Figure 13. T-Peel Strengths of Perfluoroalkylenetriazine Bonded Kapton Polyimide Laminates

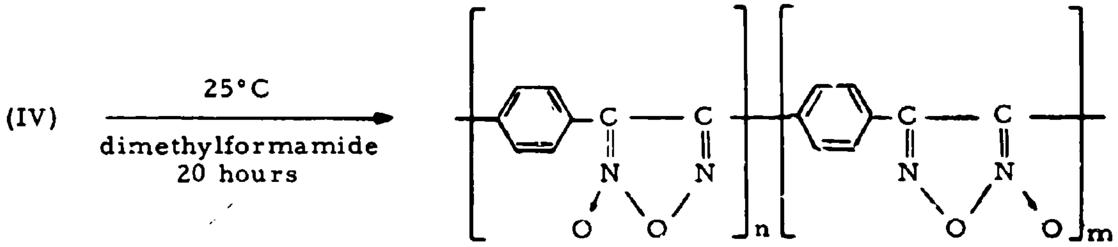
The relatively unsatisfactory adhesive performance of the tetraphenyltin cured perfluoroalkylenetriazine led us to search for an alternate cure process. One approach to achieving this objective was to synthesize terephthalonitriledioxide and evaluate it as a curing agent. Its synthesis was achieved by the following sequence of reactions.



Terephthalonitriledioxide is a nonclassical meso-ionic compound which can be considered as consisting of the three resonance hybrids shown above. When heated at 100°C for 24 hours the compound has been reported to homopolymerize as shown below.[4]



It has also been reported that, in a solution of dimethylformamide, polymerization of IV takes place at ambient temperature; however, the polymer is reported to have a structure different than that of the thermally polymerized compound.



The fact that IV is highly reactive and telomerizes readily accounts for the wide discrepancy in its published melting or decomposition temperatures.

Elemental analyses carried out on the terephthalonitriledioxide prepared at Hughes have indicated that the compound was contaminated, presumably with triethylammonium chloride, when first precipitated from solution. The latter is formed as a co-reaction product in the last step of the preparation. A single methanol wash failed to remove this impurity and a 5-minute ice water wash removed only a portion. Warm methanol-water mixtures gave the highest purity products.

The best analysis results are shown below:

Element	C, percent	H, percent	N, percent
Found	59.05	2.91	
Calc. for $C_8H_4N_2O_2$	60.00	2.52	17.50

Inadequately purified products were low in carbon (as low as 57.20 percent), high in hydrogen (as high as 3.86 percent), low in nitrogen (as low as 14.4 percent), and contained 5 percent chlorine.* Impurities did not appear to prevent the terephthalonitrile-N,N'-dioxide from functioning as a curing agent, although they did appear to adversely effect reaction rates.

Thermal stability tests conducted on the purified terephthalonitrile-N,N'-dioxide showed that it was explosive if heated suddenly above 140°C, whereas, when heated slowly to 200°C, no detonation occurred. No problems were encountered in utilizing solutions or polymer lacquers containing this material.

Many experiments were subsequently conducted to establish the efficacy with which the terephthalonitrile-N,N'-dioxide promoted cure.

In the first series of experiments, 2.5 g portions of perfluoroalkylenetriazine elastomer (Hooker Chemical Company 2572-16) were dissolved in m-bis(trifluoromethyl)benzene (22 ml), and when complete solution was achieved, a suspension of terephthalonitrile-N,N'-dioxide (E2256-41) in an equivolume mixture of bis(trifluoromethyl)benzene and ethyl acetate was added. The amount of terephthalonitrile-N,N'-dioxide incorporated was sufficient to provide solutions with 9.1, 4.8, and 2.4 percent curing agent based on the elastomer. When these solutions were heated for 3 hours at 60 ± 10°C, the sample which contained 2.4 percent curing agent gelled to a tough clear solvent-filled gum. A similar experiment in which the curing agent concentration was 1.2 percent also gelled completely in essentially the same time interval.

Five experiments then were carried out, each using 1 g of the perfluoroalkylenetriazine per 10 ml of m-bis(trifluoromethyl)benzene. A solution of terephthalonitrile-N,N'-dioxide in dioxane then was added to each polymer solution. The curing agent concentrations were 0.5, 1.0, and 2.0 percent based on elastomer. When heated for 8 hours

---

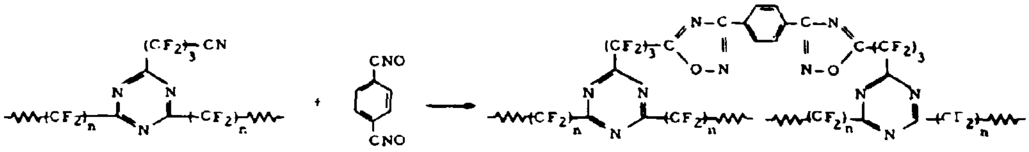
*Analyses were conducted by the Elek Microanalytical Laboratory, Torrance, California.

at 70°C, none of these solutions gelled, and it is speculated that water in the dioxane was responsible for this failure.

All subsequent experiments were carried out using solutions of the terephthalonitrile-N, N'-dioxide in bis(trifluoromethyl)benzene-ethyl acetate mixtures and in every case gelation was observed. Cures were achieved with 0.25, 0.5, 1.2, and 2.3 percent terephthalonitrile-N,N'-dioxide. In one experiment it was found that 4.8 percent terephthalonitrile-N,N'-dioxide failed to produce a cure in 3 hours at 60°C; however, when this formulation was blended with an equivalent amount of fresh elastomer to reduce the curing agent content to 2.4 percent, gelation was achieved after heating for 6 hours at 70°C and subsequently allowing the reaction mixture to set over the weekend at ambient temperature. Other freshly prepared solutions containing 2.3, 1.2, 0.5, and 0.25 percent curing agent successfully gelled within 1 to 2 hours at 70°C.

Other solutions similarly prepared contained 2.4 and 1.2 percent curing agent and formed a tough gel at ambient temperature when allowed to set over the weekend. These tests evidenced the effectiveness of a second batch of terephthalonitrile-N,N'-dioxide. Two other experiments were run at 50°C using 0.5 and 0.25 percent curing agent. The former gelled within 2 hours and the latter within 3 hours.

Thus, it has been observed that cures can be achieved with 0.25 to 2.5 percent by weight of terephthalonitrile-N,N'-dioxide based on the perfluoroalkylenetriazine elastomer, and that such cures can be achieved at ambient temperature as well as at 50 and 70°C.



Studies on terephthalonitrile-N, N'-dioxide cured perfluoroalkylenetriazine were continued to determine if improved adhesion to Kapton polyimide could be achieved. Three types of treated Kapton (5 mil thick film) were compared, namely, (1) chloroform washed, (2) alumina (325 mesh) abraded, then chloroform washed, and (3) sodium etched and acetone washed. T-peel specimens were cured at (a) 50°C for 8 hours, (b) 50°C for 8 hours followed by 100°C for 4 hours, or (c) 138 hours at 75°C. Curing agent concentrations were also varied and were 0.25 percent, 0.5 percent, 1.0 percent and 2.0 percent. Regardless of the concentration or cure conditions, no major improvements in adhesion were observed. Best results were achieved with 0.25 percent and 0.50 percent curing agent. Detailed results are shown below. Peel tests were conducted at ambient temperature.

Sample	Kapton Treatment	Cure Conditions	Peel Strength lbs/in
	At 0.25 percent curing agent		
36B1	3	c	0.11
	At 0.5 percent curing agent		
29A1	1	a	0.05
29A2	2	a	0.12
36-1	3	a	0.04
29A1	1	b	0.08
29A2	2	b	0.12
36-1	3	b	0.18
36B2	3	c	0.11

Sample	Kapton Treatment	Cure Conditions	Peel Strength lbs/in
	At 1.0 percent curing agent		
30B1	1	a	0.09
30B2	2	a	0.08
36-2	3	a	0.06
30B1	1	b	0.10
30B2	2	b	0.07
36-2	3	b	0.08
36B3	3	c	0.04
	At 2.0 percent curing agent		
34B1	1	a	0.03
34B2	2	a	0.03
36-3	3	a	0.05
34-B1	1	b	0.03
34-B2	2	b	0.07
36-3	3	b	0.09
36-B4	3	c	0.07

Experimental

Preparation of Terephthaldioxime (E2256-41). To a 3-liter round bottom flask fitted with a stirrer were added terephthalaldehyde (30 grams, 0.224 mole), hydroxylamine hydrochloride (150 grams, 1.76 moles) and water (1000 ml). A 10 percent sodium hydroxide solution (1000 ml) was added to this mixture, which was stirred for several hours. At the end of this time complete solution of the reactants was noted. The dilute basic solution then was acidified with hydrochloric acid and this precipitated the dioxime. After the dioxime was collected by filtration and air dried, it was recrystallized from ethanol to yield 24 grams of purified product, m. p. 207-208°C (65 percent yield).

Preparation of Terephthalonitrile-N,N'-dioxide (E2246-42 and -43). The preparation of terephthalobis(hydroxamic acid chloride) is based on the work of Rheinbolt, et al.[5] Thus, terephthaldioxime (20 g, 0.122 mole) was dissolved in diethyl ether (500 ml used directly without further purification). The solution was cooled to 0°C and gaseous nitrosyl chloride was passed through the mixture for 1 hour. Then the ether was removed immediately using a rotary evaporator. The solid residue was recrystallized from benzene, yielding 6 grams (24.5) percent of theory) of terephthalobis(hydroxamic acid chloride). The chloride then was dehydrochlorinated by dissolving it in dry methanol (70 g), cooling the solution to 0°C, and adding dropwise a solution of triethylamine (5.08 grams) in methanol (16 g). Upon the addition of this triethylamine solution a light tan product (5.0 grams) precipitated. This product was found to decompose when heated above 200°C. Analysis of this precipitate showed C, 58.47 percent; N, 14.39 percent; H, 3.86 percent (theory C, 60.00 percent; N, 17.50 percent; H, 2.52 percent).

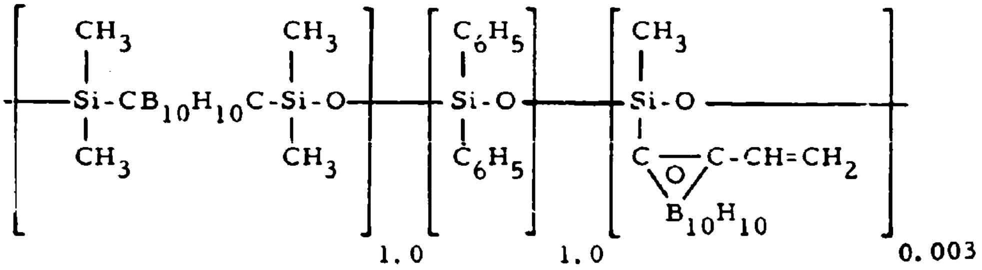
The above procedure was repeated using ether which had been dried with calcium hydride. Thus, terephthaldioxime (20.0 g) was dissolved in 500 ml of dry ether, and a stream of nitrosyl chloride gas was passed through the solution at 0°C for 1 hour. The ether then was removed immediately from the reaction mixture by distillation, and the yellow solid was recrystallized from benzene to give 6.0 grams of product (m.p. 155-165°C). This chlorinated product subsequently was dehydrochlorinated to the terephthalonitriledioxide (4.8 grams) using the procedure described previously. The solid had the following analysis:

Observed:	C, 57.86 percent; H, 3.30 percent; N, 14.87 percent; Cl, 4.97 percent
Calculated for nitrile oxide:	C, 60.00 percent; H, 2.52 percent; N, 17.50 percent

This analysis is indicative that the terephthalonitriledioxide had occluded triethylamine hydrochloride. Washing with methanol did not appear to remove any significant amounts of the triethylamine hydrochloride as indicated by a second analysis (C, 57.20 percent; H, 3.47 percent). A 5-minute ice water wash produced a somewhat better product (C, 58.28 percent; H, 3.09 percent) and indicated that a prolonged wash would be desirable. A subsequent wash in a warm methanol-water mixture (25 percent methanol) yielded a purified product having 59.05 percent carbon and 2.91 percent hydrogen.

C. SILICONE CARBORANE

Silicone carborane elastomers currently are under development at Olin Mathieson Chemical Corporation and are available in very limited quantities at a cost of approximately $100 per pound. One of these elastomers, <u>Dexsil 202</u>, has the structure shown below



This elastomer reportedly can be cured with peroxide catalysts, although very little success was achieved at Hughes using the manufacturer's recommended procedures. The material does cure, however, by prolonged heating above 200°C with or without a catalyst; consequently, extensive thermal cures have been relied upon in Hughes studies even when peroxide catalysts were incorporated. It is of interest to note that benzoic acid also is reported to promote cure. This is particularly significant because benzoyl peroxide, the manufacturer's recommended catalyst, produces benzoic acid as one of its breakdown products.

$$\phi(CO)OO(CO)\phi \xrightarrow{\Delta} 2\phi-CO_2\bullet \xrightarrow{RH} \phi-CO_2H + \phi H + CO_2\uparrow$$

Optimum high temperature oxidation resistance is reportedly obtained from Dexsil 202 when it is compounded with ferric oxide, and this compound thus has been used as a filler in many of the formulations prepared for this study.

Preliminary cure studies were performed on a 10 g sample of Dexsil 202 (lot no. X-180) that remained from a prior program. The history of this sample indicated that it did not cure to a solid state under the conditions initially recommended by Olin Chemicals. This sample was divided into three equal quantities, which were then used in subsequent formulations in an effort to establish a satisfactory cure process.

In contacts with Olin Chemicals it was learned that Dexsil 202 cures at 600°F without the addition of catalyst or accelerator and at 300°F if titanium dioxide is compounded into the polymer. In the first few experiments there was no indication that cure proceeded below 600°F, even with the peroxide catalysts. This initial cure study was performed in order to compare the curing process of the uncatalyzed material, the peroxide catalyzed material, and the titania filled, thermally cured material.

The formulations used are as follows:

		Parts by Weight
D1.	Dexsil 202 (83 percent in methyl ethyl ketone)	120
	Mapico Red No. 297 iron oxide (Columbian Carbon Co.)	10
	Min-U-Sil silica (5 micron) (Pennsylvania Glass Sand Corp.)	80
	Luperco CST (dichlorobenzoyl peroxide) (Wallace & Tiernan Inc.)	2

		Parts by Weight
D3.	Dexsil 202 (83 percent in methyl ethyl ketone)	120
	Mapico Red No. 297 iron oxide	10
	Titanox – TiO_2 (Titanium Pigment Corp.)	200
D4.	Dexsil 202 (83 percent in methyl ethyl ketone)	

The cure schedule for these formulations was:

Formulation	°F/Hours	Remarks
D1.	165/1	To drive off the methyl ethyl ketone solvent
	250/1	No polymerization
	300/8	No polymerization
	600/8	No polymerization
	600/16	Material solidified to a flexible mass
D3.	165/1	To remove solvent
	300/0.5	No polymerization was noted although Olin has reported cures at this temperature
	600/8	No polymerization
	600/16	Material solidified to a flexible mass
D4.	165/1	Solvent removal
	600/8	No polymerization
	600/16	No polymerization

It appeared from these data that under the conditions utilized, a catalyst or accelerator was required to promote cure. Thus, a satisfactory curing agent was not found which would polymerize the material at temperatures substantially lower than 600°F.

Conversations with Olin Chemicals personnel indicated that some of their customers have found that silica was a useful polymerization accelerator. Formulation D1, however, contained Min-U-Sil, a silica, and no promotion of the cure rate was observed.

It was decided to evaluate the sealant properties of formulations D1, D3, and D4, using the long term elevated temperature required to cure the polymer. A parallel effort was initiated to continue investigating techniques for decreasing the time-temperature relationship.

Once a larger sample of Dexsil 202 became available three formulations were prepared in order to evaluate the T-peel strength of Dexsil bonded Kapton film. These formulations were the same as those described earlier as D1, D3, and D4. The three Dexsil 202 systems were too viscous to apply by spraying, so they were reduced to a sprayable viscosity using benzene as a thinner.

The formulations were applied to the Kapton substrates, and T-peel panels were formed and press cured at 100 psig and 350°F for 2 hours, then 405°F for 2 hours, and finally at 600°F for 16 hours. In addition, other T-peel panels were formed, then cured in a forced air oven, rather than in a hydraulic press, with the same cure times and temperatures.

Adhesion was too poor to warrant quantitative evaluation.

Since Dexsil had not provided good adhesion for Kapton film at high temperatures in any case, an effort was made to improve its adhesive properties. Several experiments were conducted in which dimethyldichlorosilane and dimethyldiethoxysilane were used to treat the Kapton film with the expectation of modifying the film surface and making it more receptive to the Dexsil. Neither of these treatments functioned in this capacity. Etching the Kapton film with sodium-napththalene-tetrahydrofuran emulsion also failed to provide improved adhesion.

Subsequently an "additive," Dexsil 176, was provided to Hughes by an Olin representative. This additive reportedly could improve its adhesive properties and reportedly was a much higher molecular weight silicone carborane. It was formulated with Dexsil 202 as recommended and the formulation was as follows:

Dexsil 202	40 g
Dexsil 176	10 g
Fe_2O_3	0.5 g
HBO_2	2.5 g
Luperco CST	0.5 g
Xylene	100 ml

The peroxide was first dissolved in the xylene and then both Dexsils were added; Dexsil 176 did not dissolve. The suspension thus was not suitable for spray application. Ferric oxide and boric oxide subsequently were added and the mixture was heated to near boiling for 3 hours in an effort to dissolve the Dexsil 176, but to no avail. The mixture then was concentrated to a viscous state and was blended on a paint mill to achieve a more homogeneous mixture. The blended elastomer was used to coat Kapton film in subsequent work.

Other Dexsil 202 formulations which were tested are

49A-1	Dexsil 202	(100 pbw)
	Mapico Red (Fe_2O_3)	(10 pbw)
	Min-U-Sil (SiO_2)	(80 pbw)
	Luperco CST (50 percent 2,4-dichlorobenzoyl peroxide)	(2 pbw)
49A-2	Dexsil 202	(100 pbw)
	Mapico Red (Fe_2O_3)	(10 pbw)
	Min-U-Sil (SiO_2)	(100 pbw)
	Luperco CST	(2 pbw)
49A-3	Dexsil 202	(100 pbw)
	Mapico Red	(10 pbw)
	Titanox (TiO_2)	(100 pbw)
49B	Dexsil 202	(100 pbw)
	Luperco CST	(2 pbw)

Filled compositions were milled on a rubber mill and subsequently diluted with benzene to achieve a sprayable consistency. Two-ply Kapton laminates then were prepared and cured for 2 hours at 350°F, then for 4 hours at 425°F, and finally 16 hours at 600°F. Tensile peel test results on these specimens are tabulated in Table XI.

These results show that Dexsil formulations generally provided poor adhesion. The two best samples (49A2 and 49A3) in ambient temperature tests showed median values ranging from 0.03 to 0.1 pound per inch with maxima of 0.48 and 0.76 pound per inch, respectively. Values

Table XI. Results of T-Peel Tests on Silicone Carborane (Dexsil 202) Bonded Kapton Polyimide Film

		70°F Peel Tests, pounds per inch						800°F Peel Tests, pounds per inch					
		Unaged		Aged				Unaged		Aged			
				2 hours at 600°F		2 hours at 800°F				2 hours at 600°F		2 hours at 800°F	
Dexsil 202 Formulation	Kapton Film (Substrate) thickness mils	High	Median	High	Median	High	Median	High	Median	High	Median	High	Median
49A1	5	0.11	0.03					0.03	0.01				
49A2	5	0.48	0.11					0.03	0.02				
49A3	5	0.76	0.11										
49B	5	0.07	0.03	0.22	0.04	0.06	0.03	0.01	0.02	0.02		0.02	0.02
49B on dimethyldichlorosilane treated Kapton	5	0.15	0.03	0.09	0.03	0.04	0.03			0.02		0.05	0.03

dropped to near zero in the 800°F tests, however, even without high temperature aging.

Formulations which performed best at ambient temperature were those filled with titanium dioxide (approximately 50 percent by weight) and ferric oxide (~5 percent by weight) or with silica (~47 percent by weight) and ferric oxide (~5 percent by weight). Unfilled Dexsil provided the poorest adhesion. The latter formulation was also used in experiments with Kapton film pretreated with dimethyldichlorosilane, dimethyldiethoxysilane or sodium etch. Not all of these specimens were tested, however, because the adhesion often was too poor to warrant quantitative evaluation. Improvements thus were not achieved as a result of these pretreatments.

Several subsequent experiments were carried out in which additives, which were incorporated into the Dexsil 202 silicone carborane formulations, were expected to improve adhesion. These additives included vinyltriethoxysilane (Union Carbide A-151) and γ-methacryloxypropyltrimethoxysilane (Union Carbide A-174). Formulations that were prepared follow:

1.	Silicone carborane, Dexsil 202	11.9 g
	Vinyltriethoxysilane, A-151	0.63 g
	Fe_2O_3, Mapico Red 297	1.25 g
	Chlorobenzoyl peroxide, Luperco CST	0.25 g
	SiO_2, Min-U-Sil	10.0 g
	Benzene	50 ml

2.	Silicone carborane, Dexsil 202	11.9 g
	Methacryloxypropyltriethoxysilane, A-174	0.63 g
	Fe_2O_3, Mapico Red 297	1.25 g
	Chlorobenzoyl peroxide, Luperco CST	0.25 g
	Silica, Min-U-Sil	10.0 g
	Benzene	50 ml
3.	Dexsil 202	11.1 g
	A-151	0.6 g
	Mapico Red 297	1.2 g
	TiO_2 Titanox	11.7 g
	Benzene	50 ml
4.	Dexsil 202	11.1 g
	A-174	0.63 g
	Mapico Red 297	1.2 g
	Titanox	11.7 g
	Benzene	50 ml

Dried Kapton polyimide sheets that had been pretreated with sodium-naphthalene-tetrahydrofuran emulsion were subsequently spray coated with these formulations and, after drying, two ply laminates were prepared and cured at 316 °C (600°F) for 24 hours. None of these compositions provided adhesive bonds sufficiently strong to warrant quantitative testing on the Instron.

Sheeted experimental Dexsil formulations of other types were received from Olin for screening. These silicone carborane formulations were referred to as elastomeric adhesives and contain Dexsil 151 and Dexsil 176. Their exact composition was not provided; however, they undoubtedly contain HBO_2 which is added to improve adhesion. Furthermore, all of these composites except sample X-431 contained Fe_2O_3 as evidenced by their color.

The Dexsil sheets subsequently were rolled on a small hand mill to a thickness of 10 to 12 mils and then were used to bond together the plies of sodium etched Kapton film. The 2-ply laminates then were placed under a pressure of 5 psi and heated sequentially for 10 minutes at 38°C, 15 minutes at 150°C, 2 hours at 260°C, and 16 hours at 315°C. This cure schedule was recommended by the Olin Chemicals representative. Much of the elastomer squeezed out in this process; consequently, the adhesive interlayers were much thinner than the initial 10 to 12 mils, as noted in Table XII. T-peel tests were conducted on the cured laminates and the results are also shown in Table XII. The data is compared to the results of tests on a laminate obtained from Olin (X-430). It should be noted that the Olin prepared specimen had 13 ± 1 mils of adhesive (between two plys of 1 mil Kapton) whereas our specimens had 1 to 2 mils of adhesive (between plys of 5 mil Kapton). The much thinner adhesive interlayers were considered essential for practical commercial application.

Table XII. Peel Strengths of Various Silicone Carborane Bonded Kapton Polyimide Films

	73°F (23°C), lbs/in of width			Apparent Mode of Failure	400°F (204°C), lbs/in of width			Apparent Mode of Failure	Adhesive Thickness, mils
	High	Low	Median		High	Low	Median		
X-430	0.99	0.86	0.92	Adhesive					13 ± 1
X-417A	0.24	0.01	0.08	Adhesive	0.17	0.08	0.12	Cohesive	1
X-417B	–	–	Nil	Adhesive	–	–	Nil	Adhesive	1
X-417C	0.03	0.02	0.02	Adhesive	0.03	0.02	0.02	Cohesive	1
X-417D	0.03	0.01	0.02	Adhesive	0.02	0.01	0.01	Adhesive	2 ± 1
X-431	0.05	0.01	0.03	Adhesive	0.02	0.01	0.01	Cohesive	1.5 ± 0.5

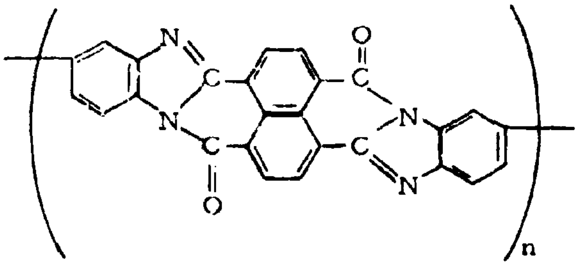
It will be noted that at 400°F three of the specimens appeared to exhibit cohesive failure rather than adhesive failure whereas at 73°F the failure was adhesive in all cases.

Dielectric properties of the silicone carboranes were very good at ambient temperature, and are shown in Table XVII.

In summary it has been found that silicone carboranes, namely Dexsil 202, Dexsil 176, and Dexsil 151, are poor adhesives for Kapton polyimide film even when the film surfaces are abraded or sodium etched. Silane type additives failed to improve adhesion. In a few cases adhesion was "satisfactory" at ambient temperature, but failed almost completely at temperatures of 200°C or above.

D. BISBENZIMIDAZOLEBENZOPHENANTHROLINE (BBB)

Bisbenzimidazolebenzophenanthroline resin (M-BBB-2, 62 g) was obtained from Dr. Van Deusen of the AFML Polymer Branch. The polymer reportedly has the following structure



Its synthesis is accomplished by reacting 3, 3'-diaminobenzidine with 1, 4, 5, 8-naphthalenetetracarboxylic dianhydride in polyphosphoric acid. Polymer used in this study had an inherent viscosity of 2.0, and consequently it was rather high in molecular weight.

Two polymer specimens (3/4 inch diameter x 1/4 inch thick) were molded at a pressure of 40,000 psi. Molding temperatures were 425°C (800°F) and 454°C (850°F), although only the latter temperature produced a satisfactory looking specimen. Attempts to mold a satisfactory specimen at 40,000 psi and 370°C (700°F) were unsuccessful, as were attempts to mold at 825°F and only 8000 psi.

The high pressures and temperatures required for molding would almost certainly eliminate this resin as a potential extrudable coating for electrical wire. Significantly lower molecular weight polymer would be needed if extrusion were to be a feasible processing technique.

Dielectric properties of the molded pellets were measured and are shown in Table XIII.

Sample 1 was molded at 454°C and sample 2 was the same molded specimen after heating for 24 hours at 100°C and subsequently cooling. Sample 3 was the specimen which was molded at 425°C. The dielectric constants and dissipation factors were very high and the insulation resistance and volume resistivity were relatively low. Although the insulation resistance and volume resistivity are not low enough to

Table XIII. Dielectric Properties of Molded BBB Pellets

Sample	Insulation Resistance at 25°C-ohms	Dielectric Constant at 1 kHz and 25°C	Dissipation Factor at 1 kHz and 25°C, percent	Volume Resistivity 500 vdc-60 sec ohm-cm
1	1.8×10^{10}	13.8	23.1	5.4×10^{10}
2	2×10^{10}	20.4	23.3	1.4×10^{11}
3	2.3×10^{10}	19.4	21.[illegible]	1.4×10^{11}

eliminate BBB resin as a potential electrical insulation material, the high dielectric constant and dissipation factors would be restrictive.

It is important to note, however, that the relatively unsatisfactory electrical properties of BBB may not be characteristic of the resin per se. This polymer is synthesized in polyphosphoric acid and thus it is quite possible that it contains a trace of residual acid in spite of the precautions taken to remove it in its entirety. This would drastically affect its electrical properties.

Efforts also were made to produce BBB films. In these experiments the polymer was dissolved in concentrated sulfuric acid to give a 4-5 percent by weight solution. The suspension was stirred for 2 days until solution was complete. Glass squares coated with this solution were subsequently immersed into diluted sulfuric acid (25, 50, or 75 percent by volume) in an effort to precipitate the polymer in film form. The following immersion sequence was used.

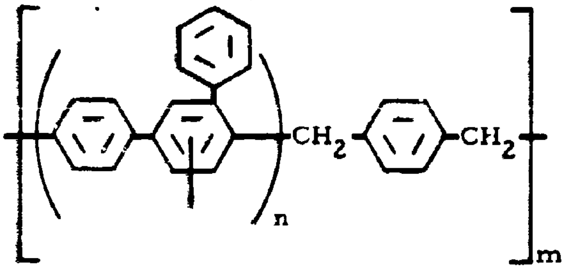
Sample				
1	75 percent acid 1 hour	50 percent acid 30 minutes	25 percent acid 90 minutes	water rinse 3 hours
2	50 percent acid 2 hours	25 percent acid 30 minutes	water rinse 3 hours	
3	25 percent acid 1 hour	water rinse 16 hours		

Each of these immersion sequences resulted in the formation of BBB films which readily peeled off the glass substrate. Furthermore, these films were relatively tough although they shrank a great deal when dried. Although no attempt was made to carry out an alkali leach, such a treatment would be necessary to remove residual acid. A process of this type appears to be feasible for preparing BBB films. Such films could be oriented upon completion of the washing processes and such orientation would probably be necessary to obtain optimum physical properties.

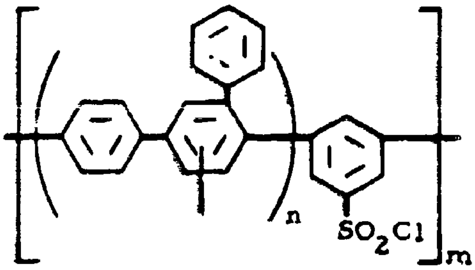
Additional work on BBB films has not been carried out primarily because such films would still require a sealant in order to make them useful as wire insulation materials.

E. POLYPHENYLENE

Polyphenylenes developed at Hughes Aircraft Company during the past five years are one of the classes of materials which warranted evaluation as potential high temperature wire insulation. These thermosetting polymers fall into two classes, namely, the xylylene glycol cured polymers and the aryl polysulfonyl chloride cured polymers. Structures of both types are illustrated below:



Type I



Type II

The first type has been scaled up to a 50 pound/lot pilot plant under a Manufacturing Technology Division sponsored program conducted jointly by Hughes Aircraft Company and Allied Chemical Company. Type I resins have been designated Abchar 412, 413, and 414 depending upon the polyphenylene: xylylene glycol weight ratio.

Type II resins are designated Abchar 912 and 913 also depending upon the polyphenylene: curing agent weight ratio. Type III resins, not illustrated, are cured with 4, 4'-biphenyldisulfonyl chloride and are designated Abchar 1112 and 1113.

Polyphenylene studies reported herein were limited to the Type I resins and both Abchar 412 and 414 were examined. Nine chloroform lacquers were prepared. These consisted of:

1. Abchar 412
2. Abchar 412 wherein 5 percent of the polyphenylene was replaced by polyphenylene oxide
3. Abchar 412 wherein 10 percent of the polyphenylene was replaced by polyphenylene oxide
4. Abchar 412 wherein 20 percent of the polyphenylene was replaced by polyphenylene oxide
5. Abchar 412 wherein 30 percent of the polyphenylene was replaced by polyphenylene oxide
6. Abchar 412 wherein 5 percent of the polyphenylene was replaced by polystyrene
7. Abchar 412 wherein 10 percent of the polyphenylene was replaced by polystyrene
8. Abchar 412 wherein 20 percent of the polyphenylene was replaced by polystyrene
9. Abchar 414

Abchar 412 prepolymer contains two parts by weight of branched fusible polyphenylene having a melting range of 160° to 220°C and a mean molecular weight of 900 ± 100 per part of xylylene glycol, whereas Abchar 414 contains four parts by weight of this fusible polyphenylene per part of xylylene glycol. In blends with polyphenylene oxide or polystyrene, the percentage of the latter was based only on the polyphenylene fraction and not on the total polyphenylene-xylylene glycol portion. Percentages, based on the blended resin, would be lower. The polyphenylene oxide and polystyrene were added in small quantities, hopefully to provide improved film forming characteristics. Furthermore, the polyphenylene oxide and polystyrene copolymerize with the polyphenylene and thus are not present as plasticizers.

All of the polyphenylene lacquers were sprayed onto abraded Kapton polyimide film for evaluation using a Paasche air brush.

Coated substrates then were air dried for approximately 4 hours at 125°F and T-peel specimens were formed by taking two of the coated substrates and bonding them with the coated surfaces together. A 3-inch length of each substrate was allowed to remain uncoated in order to leave an area which could be gripped by the jaws of the Instron Universal Testing Instrument.

T-peel specimens were then placed between glass cloth reinforced silicone rubber slip sheets and placed between the preheated platens of a hydraulic press at 350°F. A pressure of 100 psig was applied to the substrates and this pressure and temperature were maintained for 2 hours. Keeping the pressure at 100 psig, the temperature was increased to 350°F and maintained for 2 hours, then increased to 600°F and maintained for 16 hours. Heaters on the platens were then turned off and the laminated T-peel panels were left under pressure in the press until the temperatures returned to 100°F. At this point the T-peel panels were removed from the press, cut into strips 1 inch wide by 12 inches long, and submitted to the mechanical test laboratory for the determination of T-peel strengths. Results of these tests are shown in Table XIV.

Abchar 414 exhibited much poorer adhesion than Abchar 412 at both ambient and elevated temperatures. The former adhered better at 800°F than at 70°F which may have indicated further resin advancement at 800°F.

Abchar 412 exhibited the highest measurable peel strength of all resins tested at 800°F. This value dropped drastically with thermal aging, however. Efforts were also made to provide greater toughness to the polyphenylene by incorporating polyphenylene oxide or polystyrene. With both polystyrene and polyphenylene oxide there was an immediate deterioration in adhesion, both at ambient and high temperatures, as shown on page 59.

Table XIV. Results of T-Peel Tests on Polyphenylene (Abchar 412) Bonded Kapton Laminates

Sample Number	Peel Strength, lb/in width				Kapton Film Thickness, mils	Remarks
	Initial	High	Low	Median		
at 75° F						
-1	—	1.84	—	--	5	No peel—substrate failed first
-2	0.305	0.550	0.200	0.300	3	
-3	0.375	0.248	0.120	0.175	3	
-4	0.300	0.680	0.265	0.450	3	
-5	0.435	0.855	0.365	0.475	3	
-6	0.375	0.895	0.405	0.600	3	
average	0.358	0.845	0.271	0.400		
at 500° F						
-1		1.02			5	No peel—substrate failed first
-2		1.88			5	"
-3		2.04			5	"
-5		1.02			5	"
-4		1.02			3	"
-6		1.76			3	
3 mil average		1.39				
5 mil average		1.49				

	Median Values	
	At 70°F	At 800°F
Abchar 414	0.02	0.30
Abchar 412	Exceeds Substrate Strength	2.9
Abchar 412 + 5 percent polystyrene	0.84	1.5
Abchar 412 + 10 percent polystyrene	0.17	0.44
Abchar 412 + 20 percent polystyrene	0.17	0.10
Abchar 412 + 5 percent polyphenylene oxide	0.17	0.21
Abchar 412 + 10 percent polyphenylene oxide	0.21	0.18
Abchar 412 + 20 percent polyphenylene oxide	0.18	0
Abchar 412 + 30 percent polyphenylene oxide	0.21	0

It is noteworthy that 5 percent polystyrene did not have as deleterious an effect as the addition of 5 percent polyphenylene oxide, although both additives reduced the adhesive bond strengths significantly.

The excellent adhesive bond strength of polyphenylene (Abchar 412) observed at 800°F was not observed after thermal aging for 2 hours at either 600 or 800°F as shown below:

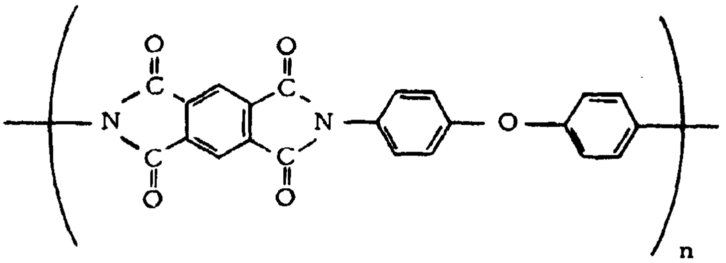
Median Values		Median Values	
Tested at 70°F		Tested at 800°F	
After 2 hours at 600°F	After 2 hours at 800°F	After 2 hours at 600°F	After 2 hours at 800°F
0.25	0.15	0.14	0.19

Dielectric tests conducted at ambient temperature on cured polyphenylene (Abchar 412) showed a dielectric constant between 2.5 and 2.9, an insulation resistance of over 10^{13} ohms and a volume resistivity of over 10^{13} ohm-cms and a dissipation factor of less than 1 percent. This data is shown in more detail in Table XVII.

Thus, although Abchar 412 has good dielectric properties at ambient temperature and good adhesion at 800°F, its loss of adhesion under high temperature aging reduces its potential value as a wire insulation. Further work is required to resolve this problem.

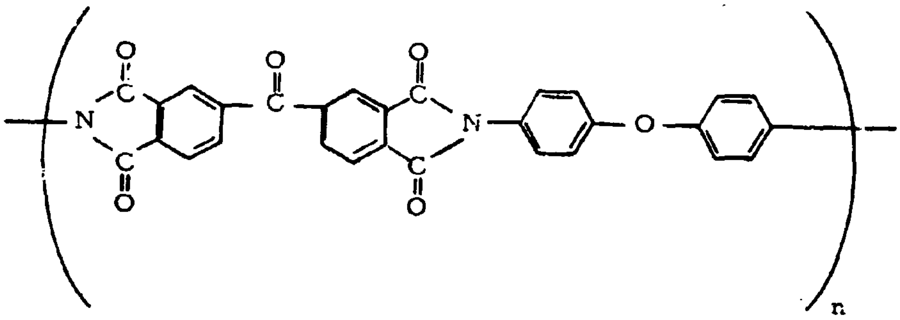
F. POLYIMIDES

Two types of polyimide, namely, Pyralin 4701 (E. I. du Pont de Nemours & Co.), and Thermadite 17 (Narmco Materials Division, Whittaker Corp.), were evaluated during this period. Both prepolymers are polyamic acids which yield polyimides when cured. The Pyralin 4701 polymer has the same structure as that of Kapton film when properly cured and this structure is shown below:



The structure of Thermadite 17 cannot be specified with certainty; however, it is analogous to the Pyralin 4701 polyimide.

A third polyimide precursor, Skybond 700 (Monsanto Co.), is believed to have the structure shown below, derived from benzophenonetetracarboxylic dianhydride and diaminodiphenyl oxide.



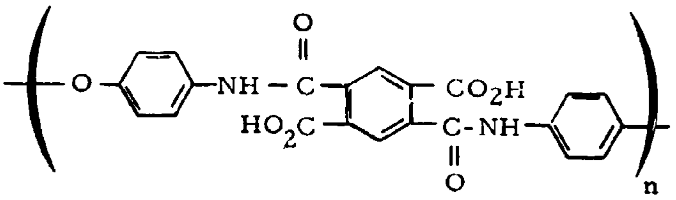
This latter resin was not evaluated during the course of our investigation since it was expected to be similar to the other polyimides in outgassing, moisture sensitivity, and adhesion.

As received, Pyralin 4701 was too viscous to apply to the Kapton polyimide film by spraying; therefore, it was reduced to a sprayable viscosity using the manufacturer's recommended solvent system, namely, two parts by volume of freshly distilled N-methylpyrrolidone to one part of xylene. The sprayable solution contained 18 g of Pyralin 4701 prepolymer per 42 ml of solvent.

This candidate sealant was sprayed onto the Kapton polyimide substrates (6 inches by 12 inches by 5 mils) and T-peel panels were formed and press cured at 100 psig in accordance with the procedure previously described for the polyphenylenes. Subsequent T-peel tests conducted on 1 inch by 12 inch laminates at temperatures up to 800°F showed that the adhesive bond strength was sufficiently great that failure did not occur prior to the failure of the Kapton substrate.

The second type of polyimide prepolymer, Thermadite 17, was also rated as a good prospective candidate sealant since prior Hughes work had indicated that this material was a promising high temperature adhesive for bonding Kapton polyimide film in another application. This prepolymer was satisfactory for spraying as received, and was applied in this manner to the abraded sheets of film. T-peel panels were then formed and press cured at 100 psig as previously described. Tests conducted at temperatures up to 500°F showed that the adhesive bond strength of this polyimide also equalled or exceeded the cohesive bond strength of the Kapton film.

Thermadite 17 and Pyralin 4701 are sold as uncyclized polyamic acid prepolymers containing both amide and carboxylic acid groups. The Pyralin 4701 is derived from pyromellitic dianhydride and 4, 4'-diaminodiphenyloxide and has the following structure prior to cure.



prepolymer

During cure, water is liberated and the polyimide is formed. The cured resin properties depend to a high degree on the efficiency with which the water can be eliminated, and the degree of success which one achieves in preventing void formation.

The large amount of water vapor evolved during cure constitutes the major problem in the utilization of polyimides as sealants. Laminates made from these resins invariably contain a large percentage of voids because the gaseous condensation products cannot escape completely during cure. Consequently, laminates having completely void free adhesive interlayers were not achieved.

Both polyimides exhibited excellent adhesion for Kapton film at ambient temperature as well as temperatures as high as 800°F. Furthermore, in most cases polyimide bonded specimens failed in the substrate rather than in the adhesive bond, although in several cases one of a set of triplicate samples in a set was observed to peel. In 800°F tests, this was primarily due to embrittlement and oxidative degradation of the Kapton polyimide substrate, whereas the adhesive interlayer was relatively protected from exposure to air and thus was subjected primarily to thermal degradation alone during the brief test period.

Dielectric properties of Pyralin 4701 are reported to be the same as those of Kapton polyimide film, since the former is the precursor or prepolymer of Kapton; however, the adhesive must be cured completely if comparable properties are, in fact, to be achieved.

T-peel strengths of various polyimide bonded Kapton laminates (2-ply) were determined using both 3-mil and 5-mil thick Kapton films. Tests were conducted at ambient temperature as well as at 500°, 600°, and 800°F. The Kapton substrates were initially 6 inches by 12 inches and the tests were conducted in accordance with ASTM test method D1876-61T. Substrates were prepared either by wet-scrubbing their surfaces with a sponge and industrial grade Ajax cleanser or were etched in a sodium-tetrahydrofuran emulsion. Following thorough scrubbing, substrates were rinsed in tap water, then in deionized water, and examined for a water break-free surface. Those panels exhibiting water breaks were recycled through the cleaning process until they were water break-free. Substrates were then dried in a forced air oven for 16 hours at a minimum temperature of 400° F and were stored in a forced air oven at 250° F until they were coated with the various candidate sealants.

Test panels were cut into 1 inch by 6 inch strips in accordance with the ASTM test method. An Instron Universal Testing Instrument was used and the jaw separation rate was set at 10 inches per minute. A portable oven was used to determine T-peel strengths at 500° F, and the radiant heat source on the Instron was used for measurements at 800° F. Results of the T-peel strength tests at 75° F and 500° F are presented in Table XV.

Table XV. T-Peel Strength of Polyimide Bonded Kapton

Polyimide	Peel Strength, lbs/in "HIGH"		Kapton Film Thickness	Remarks
	at 75° F	at 500° F		
Thermadite 17	1.49*	0.19*	5	No peel – substrates failed in all but one specimen
Pyralin 4701	1.01**	0.23**	5	No peel – substrates failed in all specimens

*Average of 5 results

**Average of 6 results

Tests were also performed at 315° C (600° F) and 427° C (800° F). In the ambient temperature and 500° F tests, specimens received no heat aging other than the normal post cure. These preliminary screening tests showed that at ambient temperature the Thermadite 17 and Pyralin 4701 both formed bonds which were as strong as the Kapton film. In subsequent tests, specimens were aged for 2 or 4 hours at 600° F or for 1 to 2 hours at 800° F. In the 800° F tests on unaged samples, failure invariably occurred in the Kapton substrate rather than in the adhesive.

On the basis of these tests it was evident that both of the polyimide adhesives tested were good high temperature adhesives for Kapton film; however, since both the Thermadite and Pyralin are polyimides similar or analogous in chemical structure to Kapton itself, they could not be expected to provide improved moisture resistance if used as a sealant. This fact, coupled with the fact that void-free adhesive interlayers cannot be achieved readily (at pressures suitable for electrical wire insulation wrapping), make the polyimides somewhat less attractive. Results of peel tests at 75°F and 800°F on thermally aged polyimide bonded Kapton films are shown in Table XVI.

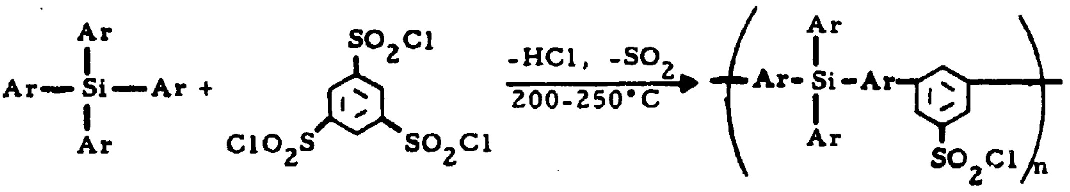
Table XVI. Results of Peel Tests on Thermally Aged Polyimide Bonded Kapton

Sealant	Kapton Film Thickness, mils	75°F Tests, pounds per inch						800°F Tests, pounds per inch					
		Unaged		Aged				Unaged		Aged			
				2 Hours at 600°F		2 Hours at 800°F				2 Hours at 600°F		2 Hours at 800°F	
		High	Median	High	Median	High	Median	High	Median	High	Median	High	Median
Pyralin 4701	5	*	*	*	*	*	*	1.0*	*	*	*	*	*
Thermadite 17	5	*	*	*	*	0.76	0.40	0.60*	*	*	*	0.33	0.21*

*Kapton substrate failed rather than adhesive. In several cases peel occurred on only one of the three samples tested as indicated by both a peel value and an asterisk.

G. POLYPHENYLSILANES

It has previously been demonstrated at Hughes that polyarylsilanes such as tetrakis(biphenylyl)silane* and diphenylbis(biphenylyl)silane* can be converted into thermosetting polymers by reaction with benzenetrisulfonyl chloride and other polysulfonyl halides. The reactions proceed as follows:



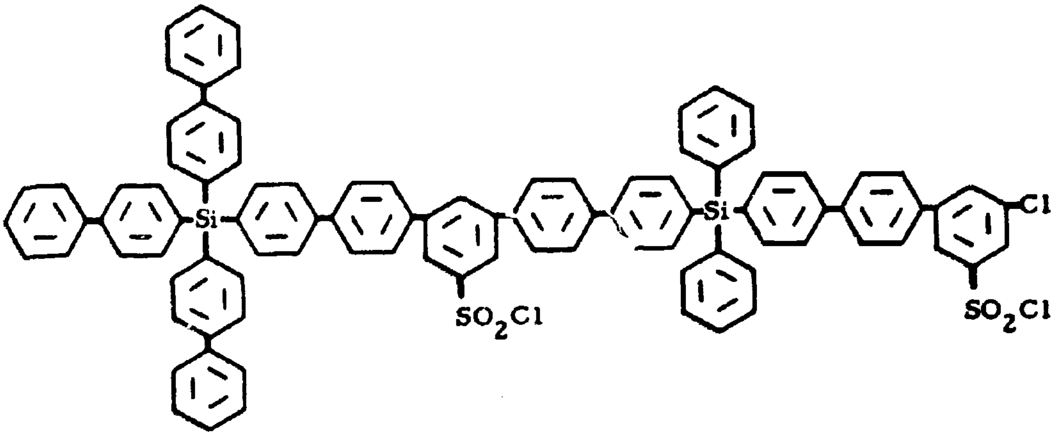
---

*This compound was obtained from Dr. Leonard Spialter of the Aeronautical Research Laboratory, Wright-Patterson AFB.

One sample of this type of polymer was prepared from an equimolar mixture of diphenylbis(biphenylyl)silane and tetrakis(biphenylyl) silane, and an analysis of the prepolymer gave the following results:

73.28 percent C, 4.48 percent H, 3.74 percent Si, 9.49 percent Cl, 6.95 percent SO_2 (by difference), $\bar{M}_n$ 1285

This analysis suggested the following structure:



The observed analysis corresponds to $C_{92}H_{67}Si_2Cl_{2.4}(SO_2Cl)_{1.6}$, which may also be expressed $C_{92}H_{67}Si_2Cl_4S_{1.6}O_{3.2}$. The structure illustrated has the empirical formula

$C_{96}H_{66}Si_2Cl_3S_2O_4$, m.w. 1509

The difference between the observed and theoretical analysis is attributed to the authenticated loss of biphenyl during the reaction (thus lowering the C and H content) and a partial loss of the remaining SO_2Cl groups. It should also be noted that some chlorination occurs in the process. This results from the coupling of aryl and chloro radicals during the SO_2 elimination process as illustrated below

$$Ar\text{-}SO_2Cl \rightarrow Ar\cdot + SO_2 + Cl\cdot \rightarrow ArCl + SO_2 \uparrow$$

A sample of the polyphenylsilane dissolved in chloroform was sprayed onto Kapton (5 mil) film, and sheets were then bonded together by curing the polymer at 100 psig and 350°F for 2 hours, then 450°F for 2 hours, and finally at 600°F for 16 hours.

Peel strengths on these specimens were too poor to warrant quantitative testing. Consequently, a new batch of tetrakis(biphenylyl) silane prepolymer was prepared. This batch of prepolymer was divided into three equal portions, and excess benzenetrisulfonyl chloride was added to serve as a crosslinking agent and hopefully to increase the molecular weight of the cured resin by chain extension. To one portion 10 percent by weight of additional benzenetrisulfonyl chloride was added (based on the initial benzenetrisulfonyl chloride used), to a second portion 20 percent excess was added, and to the third portion 40 percent excess was added.

Kapton polyimide laminates prepared from the blended resins were cured at 260°C (500°F) for 16 hours. However, bond strength of these laminates was also too low to warrant quantitative testing. Too little is known about the polymer synthesis procedure to permit the selection of proper cure conditions, and it is quite apparent that the synthesis process must be studied more comprehensively before the polyphenylsilanes can be evaluated properly. It is quite possible that the polyphenylsilane adhesive interlayer simply was too thin or that too large an excess of benzenetrisulfonyl chloride had been used.

Experimental

(C2813-51). A solution of 1, 3, 5-benzenetrisulfonyl chloride (7. 5 g, 0. 02 mole) and tetrakis(biphenylyl)silane (12. 8 g, 0. 02 mole) in chloroform (100 ml) was heated at reflux for about 16 hours. Solvent then was removed and the reactants were heated, under argon, from 205 to 245°C over a 70 minute period, then at 210° ± 10°C for 7 hours, and finally at 230° ± 5°C for 8 hours. The polymeric product weighed 12.3 g. Biphenyl (0.6 g) sublimed from the reaction mixture.

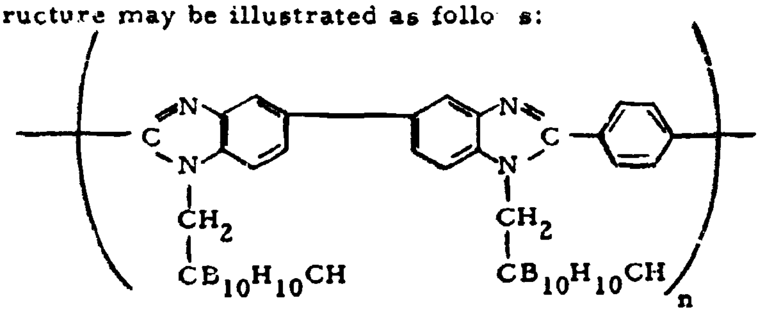
(C2813-51). A solution of tetrakis(biphenylyl)silane (14.1 g, 0.022 mole), diphenylbiphenylylsilane (3.9 g, 0.008 mole), and benzenetrisulfonylchloride (11.2 g, 0.03 mole) in chloroform (150 ml) was heated at reflux for 16 hours and then the solvent was removed under vacuum. The dried reactants were heated to 235 ± 5°C and stirred continually under argon for 24-3/4 hours. The polymer weighed 16.3 g and the sublimed biphenyl weighed 0.8 g.

H. CARBORANE MODIFIED POLYBENZIMIDAZOLE

A sample of carborane modified polybenzimidazole prepared at the Thiokol Chemical Corp. was obtained from AFML as a 2 percent solids lacquer. This lacquer was applied to clean Kapton polyimide film by spraying. Coated specimens then were bonded together to yield T-peel sandwiches which were press cured at 100 psi in accordance with the schedule described for the polyphenylenes elsewhere in this report.

This polymer has been reported to be highly superior to conventional polybenzimidazole in thermal degradation studies conducted in air at temperatures over 500°C.

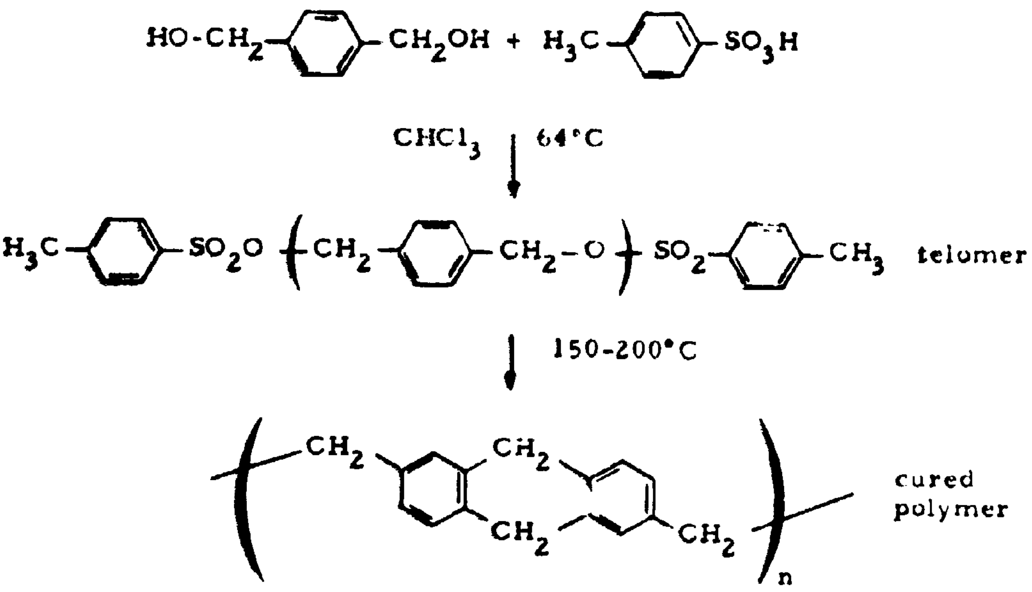
Its structure may be illustrated as follows:



The cured T-peel specimens prepared as described exhibited very poor adhesion. However, this may be due to a resin deficiency since very little polymer was available for evaluation. Furthermore, too little material was available to permit subsequent experiments and an investigation of suitable cure procedures.

I. POLYXYLYLENE

Polyxylylene is a polymer derived from xylylene glycol. A telomeric precursor of this compound is the intermediate used in curing Abchar 412 type polyphenylenes. Polyxylylene is prepared by the reaction of xylylene glycol with toluenesulfonic acid, as illustrated below:



The prepolymer was evaluated as an adhesive because its relative stability in cured polyphenylenes suggested that it might have good high temperature properties by itself.

Dielectric properties were not measured on the resin because it failed to exhibit useful adhesive properties at either ambient temperature or 800°F. Results of T-peel tests on polyxylylene bonded Kapton polyimide film are shown below:

Sealant	Kapton Film thickness-mils	70°F Peel Tests, pounds per inch						800°F Peel Tests, pounds per inch			
		Unaged		Aged				Aged			
				2 Hours at 600°F		2 Hours at 800°F		2 Hours at 600°F		2 Hours at 800°F	
		High	Median	High	Median	High	Median	High	Median	High	Median
Polyxylylene	5	0.07	0.04	0.27	0.20	0.22	0.13	0.17	0.05	0.07	0.04

III. ELECTRICAL PROPERTIES MEASUREMENTS

Electrical properties of the various high temperature polymers investigated herein are summarized in Table XVII. Data on polyphenylene (Abchar 412, Hughes Aircraft Company), "Pyrrone" resin (type I, Hughes Aircraft Company), bisbenzimidazolebenzophenanthroline (BBB, AFML Polymer Branch) and perfluoroalkylenetriazine (Hooker Chemical Co.) were determined at Hughes, whereas the properties of "Pyrrone" resin (types II and III) were obtained from NASA Langley, and the properties of perfluoroalkylenetriazine (Dow Corning), Kapton polyimide (du Pont), Dexsil 202 (silicone carborane, Olin Chemicals) and Pyralin 4701 (polyimide prepolymer, du Pont) were collected from AFML reports, from manufacturer's data sheets, or verbally from manufacturer's representatives. Pyralin is a prepolymer which cures to a polyimide having the same structure as Kapton film, and consequently its dielectric properties are reportedly the same as those of Kapton film, provided, of course, that complete cure is achieved. When used as an adhesive for Kapton film, water of condensation cannot necessarily be removed completely, and consequently the dielectric properties of the interlayer can be inferior to the Kapton film itself.

Standard ASTM procedures were used in all tests carried out at Hughes. However, the recommended sample sizes could not be used in a few cases. Dielectric constants and dissipation factors were determined by ASTM procedure D150. For these tests 1.9-inch diameter by 1/8-inch thick specimens are recommended and such samples were used for the "Pyrrone" resin. BBB resin could not be molded to this size because of the combined high temperature (454°C, 840°F) and high pressure (40,000 psi) required; consequently, a 3/4-inch diameter by 1/4-inch thick specimen was tested. Insulation resistance and volume resistivity were determined by ASTM procedure D257.

A comparison of the dielectric property data indicates that BBB resin had the poorest dielectric properties of any of the materials studied. As noted in the discussion of the BBB resin this may not be characteristic of the resin per se, but may be an indication that the resin was

Table XVII. Electrical Properties of Various Polymers

Polymer	Insulation Resistance (ohms) at 500 vdc -25° C	Volume Resistivity ohm cm at 25° C 500 vdc	Dielectric Constant 25° C	Dielectric Strength	Power Factor	Dissipation Factor, 25°C Percent
Polyphenylene (Abchar 412) Hughes Aircraft Company	$>10^{13}$	$>10^{13}$	2.5 to 2.9 at 1 kHz			0.1 to 0.7
Pyrrone (Type I)°; this type was used in the T-peel tests	$>10^{13}$‡‡	3×10^{14}‡‡	3.2‡‡			1.2
Pyrrone (Type II)* (NASA-Langley)		10^{16}	6.5 at 10^2 to 10^5 Hz	10^6 volts/cm at 25°C	0.002 at 30 to 150°C 10^4 Hz	
Pyrrone (Type III)°° (NASA-Langley)			2.3 at 20 to 300° C 10^2 to 10^5 Hz		0.002 at 20 to 140° C 10^4 Hz	
M-BBB-2 (AFML-polymer branch)	2×10^{10}	1.4×10^{11}	18			22
Kapton film (Dupont)		10^{18} at 25° C 10^{17} at 100° C 10^{14} at 200° C 10^{11} at 300° C (all at 125 volts)	3.6 at 25 to 300° C	3000 volts/mil 25 to 200°C; 1500 volts/mil at 300°C		0.1 to 0.2 at 25° to 200°C
Perfluoroalkylene-triazine (Type I) (Dow Corning)		2×10^{13}***	2.0***	363 volts/mil (227 after 24 hours in H_2O)		1.5***
Perfluoroalkylene-triazine (Type II) (Dow Corning)		9×10^{13}***	2.4***	433 volts/mil (216 after 24 hours in H_2O)		2.0***
Perfluoroalkylene-triazine (Hooker Chemical Co.)	3×10^{12}	1×10^{14}	1.8			0.6
Silicone carborane (Dexsil 201)		5×10^{15}	1.5 ‡‡‡	1500 volts/mil on 1 mil film		0.6
Polyimide (Pyralin 4701)		10^{18}	3.6	3000 volts/mil at 25 to 200° C		0.1 to 0.2

°Derived from tetraethyl ester of benzophenonetetracarboxylic acid and 3,3'-diaminobenzidine.

°°Derived from pyromellitic dianhydride and diaminobenzidine.

***No significant change after 24 hours in water at 25° C.

*Derived from benzophenonetetracarboxylic dianhydride and 3, 3'-diaminobenzidine.

‡‡No significant change after setting 4 days over water or after 60 hours (2-1/2 cycles) at a 95 percent relative humidity and a temperature cycle ranging from 75 to 160° F.

‡‡‡This value probably is erroneous.

contaminated with a trace of phosphoric acid, the solvent used in its synthesis. All other resins had volume resistivities over 10^{13} ohm-cm.

Dielectric constants of Dexsil silicone carborane (1.5) and perfluoroalkylenetriazine (1.8) were exceptionally low. The latter value, determined on the Hooker Chemical Co. polymer, is somewhat lower than, but rather close to, that reported by the Dow Corning Corporation on its type I perfluoroalkylenetriazine.

Dissipation factors (loss tangents) were lowest on polyphenylene and Pyralin 4701 polyimide, although the Dexsil silicone carborane and perfluoroalkylenetriazine were rather close. "Pyrrone" resin (type I) and the Dow Corning perfluoroalkylenetriazines were in the range of 1.2 to 1.5 percent, which is certainly within a useful range. Only the BBB resin value was excessive.

Dielectric properties of "Pyrrone"- Kapton insulated wire depend upon the processing conditions, and the reader should refer to the section of this report which discusses "Pyrrone" for wire data.

Three dielectric specimens were prepared from Epon 828 (Shell Chemical Company) and triethylenetetramine (10.7 percent by weight) in order to determine the effect of sample size on properties. Samples were cured 4 hours at 70°F, then postcured 2 hours at 165°F (74°C). This data was desired to prove that sample size was not a significant variable in our test fixture. Only minor variations were found as shown in Table XVIII.

Table XVIII. Dielectric Properties of an Epoxy Resin Relative to Sample Size

Property	Specimen Number and Size		
	1	2	3
	1/4" x 1" diameter	1/4" x 1.9" diameter	0.075"x1.9" diameter
Tested without grease or aluminum foil coating			
Dielectric constant	3.96	89	3.96
Dissipation factor, percent	0.90	0.87	0.91
Insulation resistance, ohms	5×10^{12}	5×10^{12}	5×10^{12}
Volume resistivity, ohms-cm	4.28×10^{13}	1.37×10^{14}	4.68×10^{14}
Coated each side of the specimen with aluminum foil			
Dielectric constant	3.89	3.92	4.00
Dissipation factor, percent	0.92	0.86	0.90
Insulation resistance, ohms	5×10^{12}	5×10^{12}	5×10^{12}
Volume resistivity, ohms-cm	4.28×10^{13}	1.37×10^{14}	4.68×10^{14}
Coated with a film of silicone grease and aluminum foil			
Dielectric constant	3.96	3.92	4.04
Dissipation factor, percent	0.90	0.86	0.89
Insulation resistance, ohms	5×10^{12}	5×10^{12}	5×10^{12}
Volume resistivity, ohms-cm	4.28×10^{13}	1.37×10^{14}	4.68×10^{14}

IV. REFERENCES

1. V.L. Bell and G.F. Pezdirtz, Polymer Letters, 3, 977-984 (1965): Amer. Chem. Soc. Polymer Preprints, 6, September 1965.

2. J.G. Colson, R.H. Michel, and R.M. Paufler, J. Poly. Sci. 4, A-1, 59-70 (1966).

3. F. Dawans and C.S. Marvel, J. Poly. Sci. 3, A; 3549-3571 (1965).

4. Overberger, C.G. and Fujimoto, S., Polymer Letters, 3, 735-738 (1965).

5. Rheinboldt, H., Dewald, M., Jansen, F., and Schmutz-Dumont, O., Ann., 451, 161-178 (1926).

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Hughes Aircraft Company
Centinela and Teale Streets
Culver City, California 90230

2a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b. GROUP

3. REPORT TITLE
HIGH TEMPERATURE ELECTRICAL WIRE COATINGS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Interim Report — 1 Feb 1968 — 1 Feb 1969

5. AUTHOR(S) (First name, middle initial, last name)
Norman Bilow
Kenneth L. Rose

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
May 1969	85	5

8a. CONTRACT OR GRANT NO.
F33615-68-C-1322

b. PROJECT NO.
7340

c.
Task No. 734007

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
AFML TR-69-111, PART I

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10. DISTRIBUTION STATEMENT This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made ONLY with specific prior approval of the Elastomers and Coatings Branch, MANE, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio

13. ABSTRACT

The purpose of this research was to develop new and improved polymeric coatings for electrical wires which are stable to temperatures above 500° F (up to 800° F) for use on future high speed (greater than Mach 3) aircraft and missile systems.

Polyimidazopyrrolone ("Pyrrone"), perfluoroalkylenetriazine, silicone carborane, bis-benzimidazolebenzophenanthroline (BBB), polyphenylene, two polyimides, polyphenylsilane, carborane modified polybenzimidazole, and polyxylylene were investigated as potential high temperature polymeric wire coating materials. "Pyrrone" and the two polyimides were found to be excellent adhesives for Kapton polyimide film, whereas the silicone carborane and perfluoroalkylenetriazine showed poor adhesion for Kapton. Polyphenylene (Abchar 412) also showed excellent adhesion for Kapton but lost this adhesion under high temperature thermal aging.

"Pyrrone", perfluoroalkylenetriazine and silicone carborane all had very good dielectric properties. "Pyrrone" has been successfully used as a Kapton sealant and wires containing this combination have survived 28 day humidity tests at 95 percent RH at 185° F without peeling. Such wires had poorer dielectric properties when wet, but regained their properties when redried. Dielectric properties of the "Pyrrone"-Kapton combination depended upon the cure process used; however, a good reproducible cure cycle has been developed. A new cure process for perfluoroalkylenetriazine elastomer was discovered which functions at ambient temperature or higher. Cures were achieved in 2 days at 25° C, in 2 to 3 hours at 50 to 60° C or almost instantly at 150° C. The curing agent is terephthalonitrile-N, N'-dioxide and is effective in concentrations of 1/4 to 2-1/2 percent. Elastomer cured by this curing agent is far more resistant to moisture than the tetraphenyltin cured elastomer. Investigation of the triazine polymer cured by this improved process is continuing.

This abstract is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made ONLY with specific prior approval of the Elastomers and Coatings Branch, MANE, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Electrical Wire						
High Temperature Polymeric Insulation						
Wire Coatings						
Insulation						
Polyimidazopyrrolone						
Perfluoroalkylenetriazine						
Silicone Carborane						
Polyphenylsilane						
Curing Agent						
Polyimide						
Pyrrone						

UNCLASSIFIED
Security Classification