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HIGH TEMPERATURE POLYIMIDES FOR ELECTRICAL EQUIPMENT

By Bobby W. Kennedy
Astrionics Laboratory

NASA

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Huntsville, Alabama*

TECHNICAL MEMORANDUM X-53523

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ABSTRACT

Polyimide materials, such as H-film* (pyromellitic dianhydride), molding compounds, and adhesives, that can be used in electronic equipment and withstand space and lunar environments have been studied.

H-film, a polyimide with the ability to maintain its physical, electrical, and mechanical properties over a wide temperature range, is expected to withstand the high vacuum on the moon. H-film has a chain of rings in its skeleton instead of a single chain. The carbon ring absorbs energy without degradation; whereas under the same conditions, a single chain would rupture.

The adhesive systems used in laminating H-film will have approximately the same properties as H-film. An example is benzophenoneteracarboxylicdianhydride (BTDA) reacted with oxydianiline (ODA) in which the thermal stability appears to be similar to that of H-film. This adhesive system decomposes within 20 hours at 400°C. It shows relatively small weight losses at 300°C during the same period.

Experiments indicate that the most promising adhesive system is the one derived from BTDA and ODA. Films can be deposited from solutions, and powders can be molded into articles varying from very tough and flexible to very hard and brittle with thermal stabilities ranging from 260 to 430°C. The use of carborane in polyimides will be particularly beneficial in processing the end product and for thermal stability. The carborane groups should increase solubility in common solvents and decrease the flow point. Both factors will greatly enhance processing.

Polyimide materials may be obtained in granular molding compounds for use in compression molding. This fast curing compound has extremely soft flow and approximately the same physical properties as H-film.

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*E. I. du Pont de Nemours and Co., Inc. registered trademark. Name has been changed to Kapton.

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

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HIGH TEMPERATURE POLYIMIDES FOR ELECTRICAL EQUIPMENT

By

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Prototype Development Branch
Astrionics Laboratory
Research and Development Operations

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HIGH TEMPERATURE POLYIMIDES FOR ELECTRICAL EQUIPMENT

SUMMARY

Polyimide materials, such as H-film* (pyromellitic dianhydride), molding compounds, and adhesives, that can be used in electronic equipment and withstand space and lunar environments have been studied.

H-film, a polyimide with the ability to maintain its physical, electrical, and mechanical properties over a wide temperature range, is expected to withstand the high vacuum on the moon. H-film has a chain of rings in its skeleton instead of a single chain. The carbon ring absorbs energy without degradation; whereas under the same conditions, a single chain would rupture.

The adhesive systems used in laminating H-film will have approximately the same properties as H-film. An example is benzophenonctetracarboxylicdianhydride (BTDA) reacted with oxydianiline (ODA) in which the thermal stability appears to be similar to that of H-film. This adhesive system decomposes within 20 hours at 400° C. It shows relatively small weight losses at 300° C during the same period.

Experiments indicate that the most promising adhesive system is the one derived from BTDA and ODA. Films can be deposited from solutions, and powders can be molded into articles varying from very tough and flexible to very hard and brittle, with thermal stabilities ranging from 260 to 430° C. The use of carborane in polyimides will be particularly beneficial in processing the end product and for thermal stability. The carborane groups should increase solubility in common solvents and decrease the flow point. Both factors will greatly enhance processing.

Polyimide materials may be obtained in granular molding components for use in compression molding. This fast curing compound has extremely soft flow and approximately the same physical properties as H-film.

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INTRODUCTION

The objective of the work being done in polyimides is to develop an adhesive for laminating H-film flat conductor cables.

The information on H-film* was obtained from the E. I. du Pont de Nemours and Co., Inc; no tests were performed by the Prototype Development Branch. The H-film section is included so the development of polyimide adhesive film by NASA and Quantum, Inc. may be more completely understood.

Avionic components must be stable to withstand space and lunar environments. These components will be subjected to the estimated -184° C temperature of the lunar night, with rapid transition to the 138° C of the lunar day. During the high temperature of the lunar day, there is no air to provide convection cooling (the vacuum of the moon is estimated at approximately 1.33×10^{-10} N/m^2). Under these high-temperature vacuum conditions, there is danger of plastics used in electronic packaging and wire insulation outgassing, with the possibility that material may condense on the optics of television cameras and electrical contacts. Under the low temperature environment, there is danger of breakage in cables and insulating materials that undergo flexing and vibration.

H-film, a material of high molecular weight that can be produced in film form, was selected in a basic approach to producing material that would meet the stringent environmental requirements. H-film is a polyimide, resulting from the polycondensation reaction between an aromatic tetrabasic acid and an aromatic diamine. Because of a unique combination of physical, chemical, thermal, and electrical properties, H-film will be of value as high temperature insulation and in various other applications in the space and electronics field.

The H-film polyimide is called a ladder polymer. Instead of having a single chain as its skeleton, it has a chain of rings. These rings distribute energy all around the ring rather than by the individual atom that is hit (as in the carbon-carbon skeleton), thus making H-film stable.

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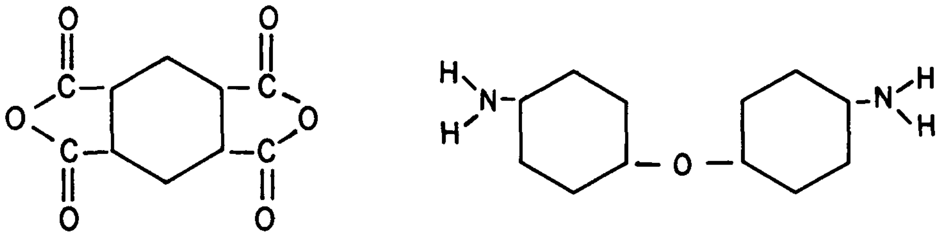
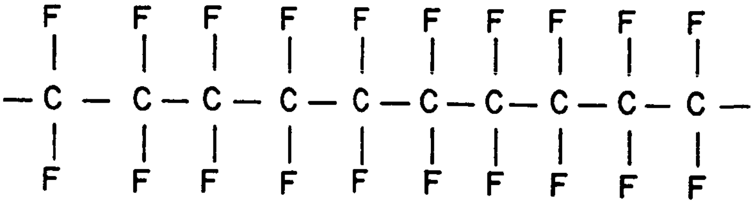
*E. I. du Pont de Nemours and Co., Inc. registered trademark. Name has been changed to Kapton.



H-film reactants

Perfluorocarbons have the same basic carbon-carbon skeleton; all the fluorine groups that are attached shield them from attack and attachment. This accounts for many of their unusual properties.



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Polytetrafluoroethylene

POLYIMIDE H-FILM

The ability of H-film polyimide to retain its excellent physical, electrical, and mechanical properties over a wide temperature range has resulted in new design and application concepts in film technology. This is especially true for high temperature applications.

H-film has been used successfully over a temperature range from -269 to 400° C. At room temperature the properties of Mylar* polyester film and H-film are similar; however, the properties of H-film are less affected by

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*E. I. du Pont de Nemours and Co., Inc. registered trademark.

temperature variations than those of Mylar. A flame resistant material, H-film begins to char above 800°C. There is no known organic solvent for H-film; it is infusible.

Some applications for H-film are: (1) wire and cable wrap, (2) motor slot liners, (3) formed coil wrap, (4) transformers, (5) capacitors, (6) flexible printed circuits, (7) magnetic and pressure sensitive tapes, (8) hose and tubings, (9) flat conductor cables, and (10) multilayer printed circuits. Some H-film applications are shown in Figure 1. Many applications are based on the fact that H-film electrical properties, such as dielectric strength and dissipation factor, remain nearly constant over a wide range of temperature and frequency. Other applications make use of its radiation or chemical resistance at high temperatures.

Ladder Polymers

When a new type of electrical insulation is formulated, many of its properties are determined by extrapolation with other materials that have similar chemical structures, and the knowledge of the differences in their chemical structures. For example, polyvinylchloride, polyethylene, polystyrene, and polypropylene all have the same basic carbon-carbon chain structure; the differences being in the chemical groups attached to or branching off from that basic chain.

The ladder polymers (Fig. 2) are a chain of polyhedra, often hexagons. Perfluorocarbon, silicone, and polyimide materials have become available. The perfluorocarbons have the same basic carbon-carbon skeleton. The fluorine groups that are attached shield them from attack. The silicones have a different skeleton structure. More energy is required to rupture the silicone-oxygen bond than the carbon-carbon bond. The monomers or reactants for these polymers are different from other polymeric precursors in that (1) they are all ring rather than chain structures; and (2) instead of having a reactive head and tail that can link with other heads and tails to form the conventional polymer, they have in effect at least two heads and tails so that the ladder structure can grow without any weak links.

An advantage of a ring structure is that, when it is hit with an overload of energy (heat or radiation), the energy is distributed all around the ring and absorbed by the ring rather than by the individual atom that is hit. The same amount of energy hitting a long chain structure will usually cause rupture or scission, while a ring structure often absorbs it without degradation. This property accounts for the exceptional radiation resistance and thermal stability of ladder polymers, and also explains their flexibility at cryogenic temperatures and lack of a melting point at elevated temperatures.

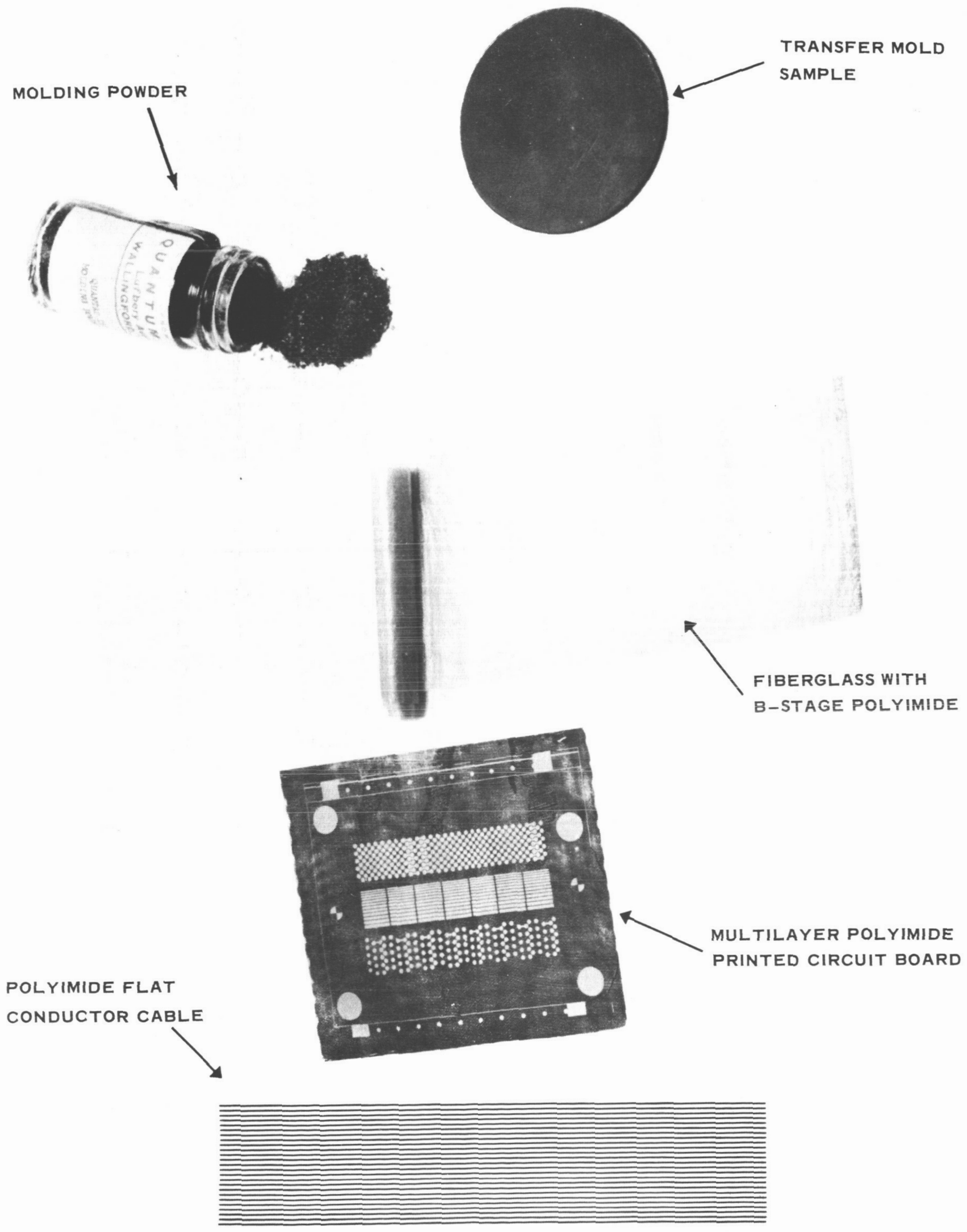
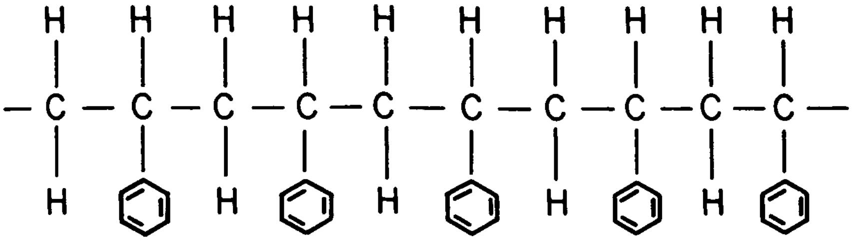
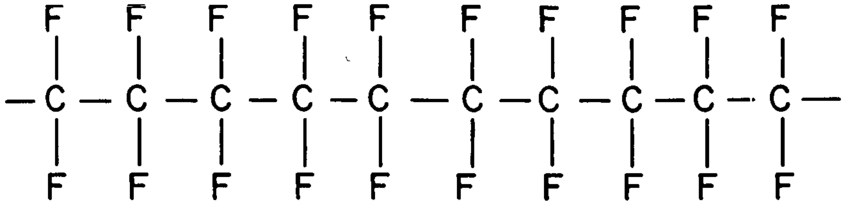


Figure 1. H-Film Applications



POLYSTYRENE



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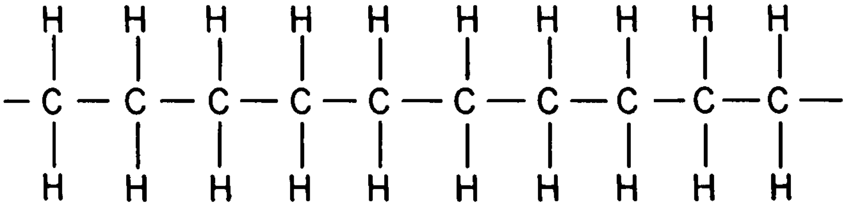
POLYTETRAFLUOROETHYLENE



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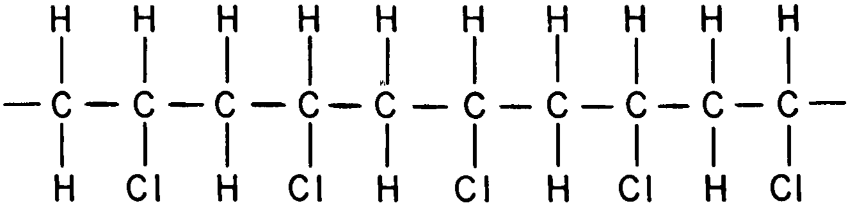
POLYETHYLENE



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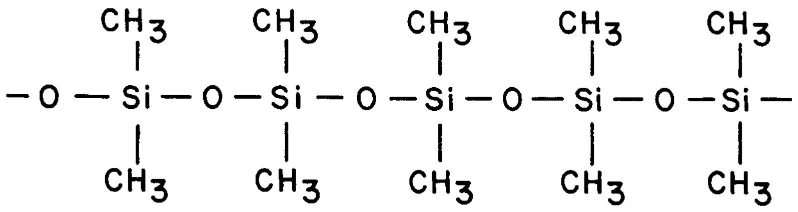
POLYVINYL CHLORIDE

Figure 2. Ladder Polymers



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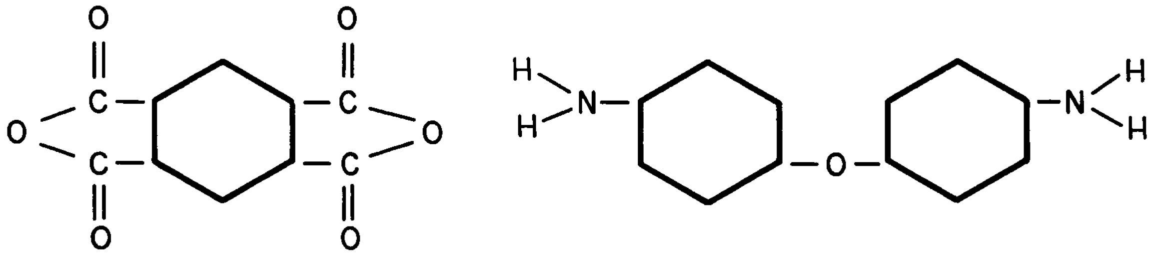
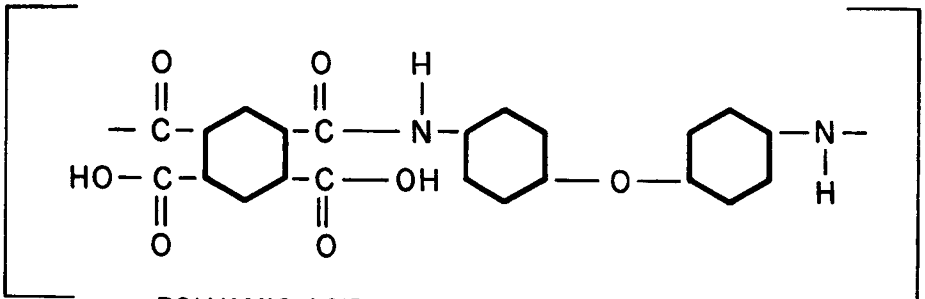
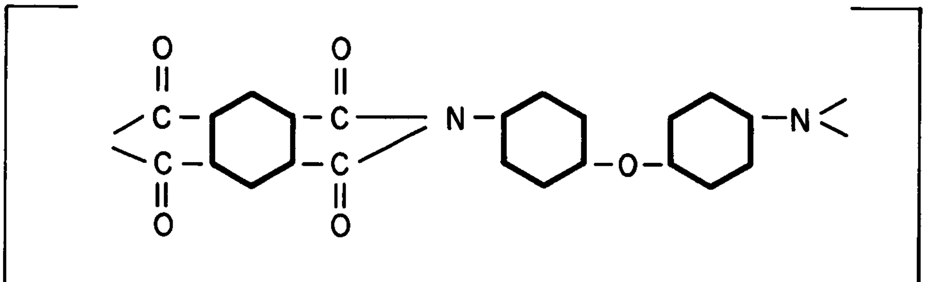
SILICONE



REACTANTS FOR POLYIMIDE



POLYAMIC ACID



POLYIMIDE

Figure 2. Ladder Polymers (Cont'd)

Although the polyimides are one of the first examples of ladder polymers to become commercially available, others are made. Several years ago, the General Electric Company was issued a patent on a silicone that possessed a ladder structure. Normco Corporation developed a ladder type laminating resin named "Imidite." Development research has been reported on other ladder polymers from Westinghouse Corporation and the University of Iowa.

H-Film Properties

H-film is a tough, golden-yellow film having the following properties:

Solvent (organic)	None known
Sodium hydroxide (100° C)	Solvent
Melting point	None
Specific gravity	1.4
Moisture up-take (50 percent relative humidity)	1.3 percent
Service life aged in air	
200°C	Indefinite
250°C	8 years (extrapolated)
275°C	1 year (extrapolated)
300°C	3 months
400°C	12 hours
Zero strength temperature	
(1.38×10^5 N/m^2 load, 5 seconds to failure)	815°C

Tensile strength (Fig. 3)	
25°C	1.73×10^{8} N/m^{2}
200°C	1.17×10^{8} N/m^{2}
Tensile modulus (Fig. 4)	
25°C	2.96×10^{9} N/m^{2}
200°C	1.79×10^{9} N/m^{2}
Elongation at break (Fig. 5)	
25°C	70 percent
200°C	90 percent
Tear strength	
25°C	315 kg/m
Dielectric constant (Fig. 6)	
10^{3} Hz/25°C	3.5
10^{3} Hz/200°C	3.0
Dissipation factor (Fig. 6)	
25°C	0.003
200°C	0.002
Dielectric strength (Fig. 7)	
25°C	260 kV/mm
Volume resistivity ohm-cm (Fig. 8)	
25°C	10^{18}
200°C	10^{14}
Surface resistivity (ohms)	
25°C, one kV, 50 percent humidity	10^{16}

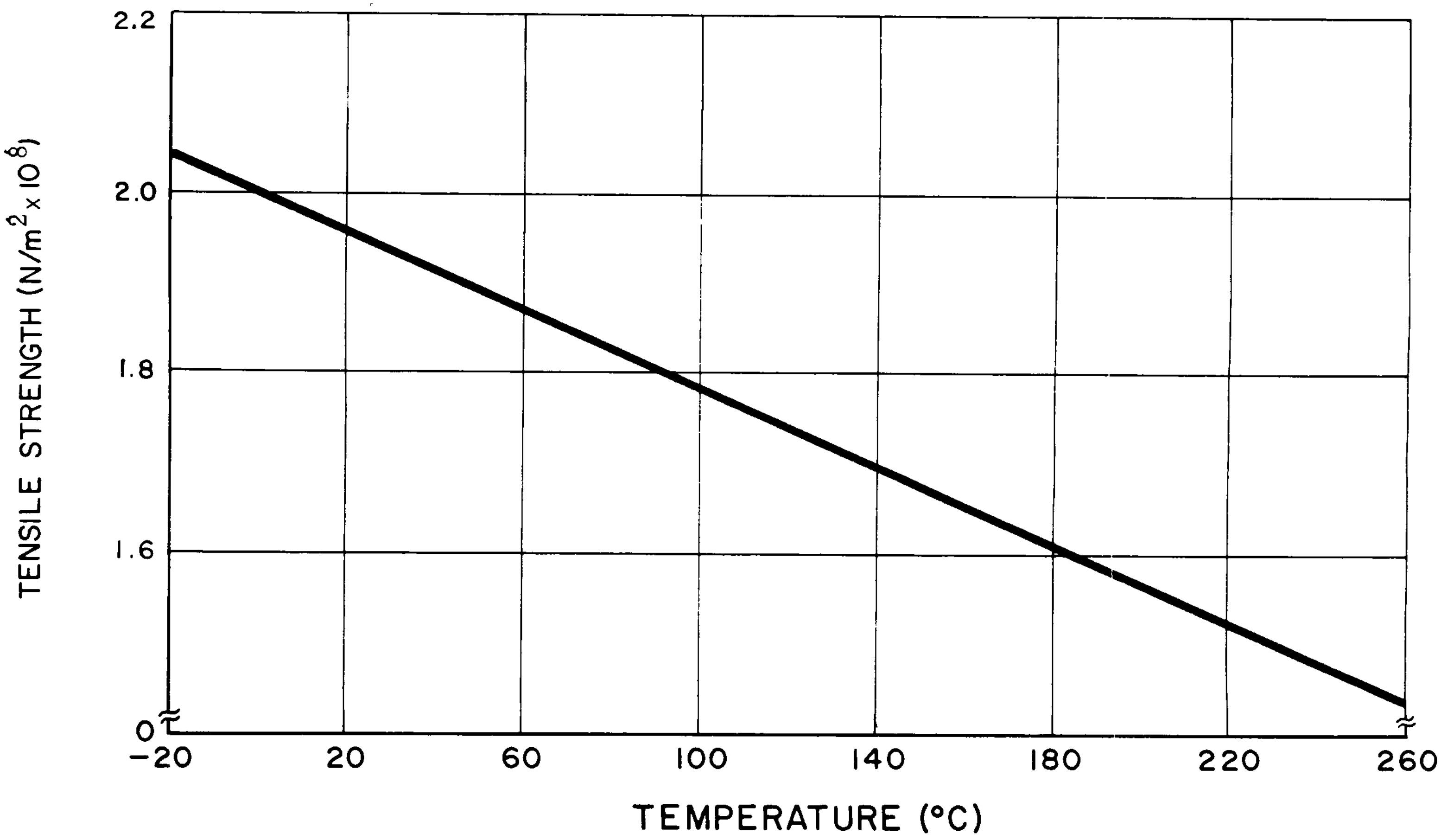


Figure 3. H-Film Tensile Strength Versus Temperature (Typical)

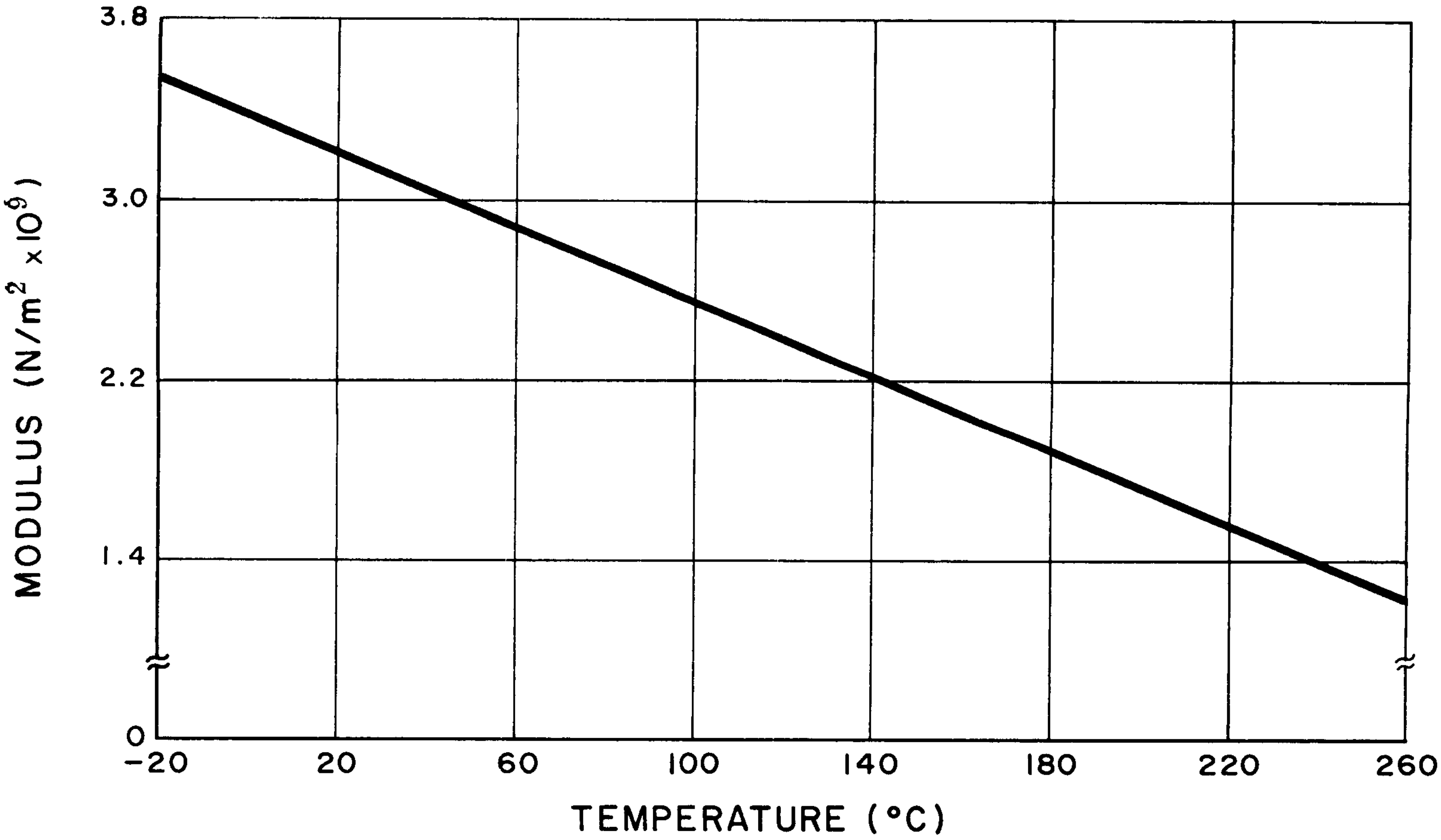


Figure 4. H-Film Modulus Versus Temperature (Typical)

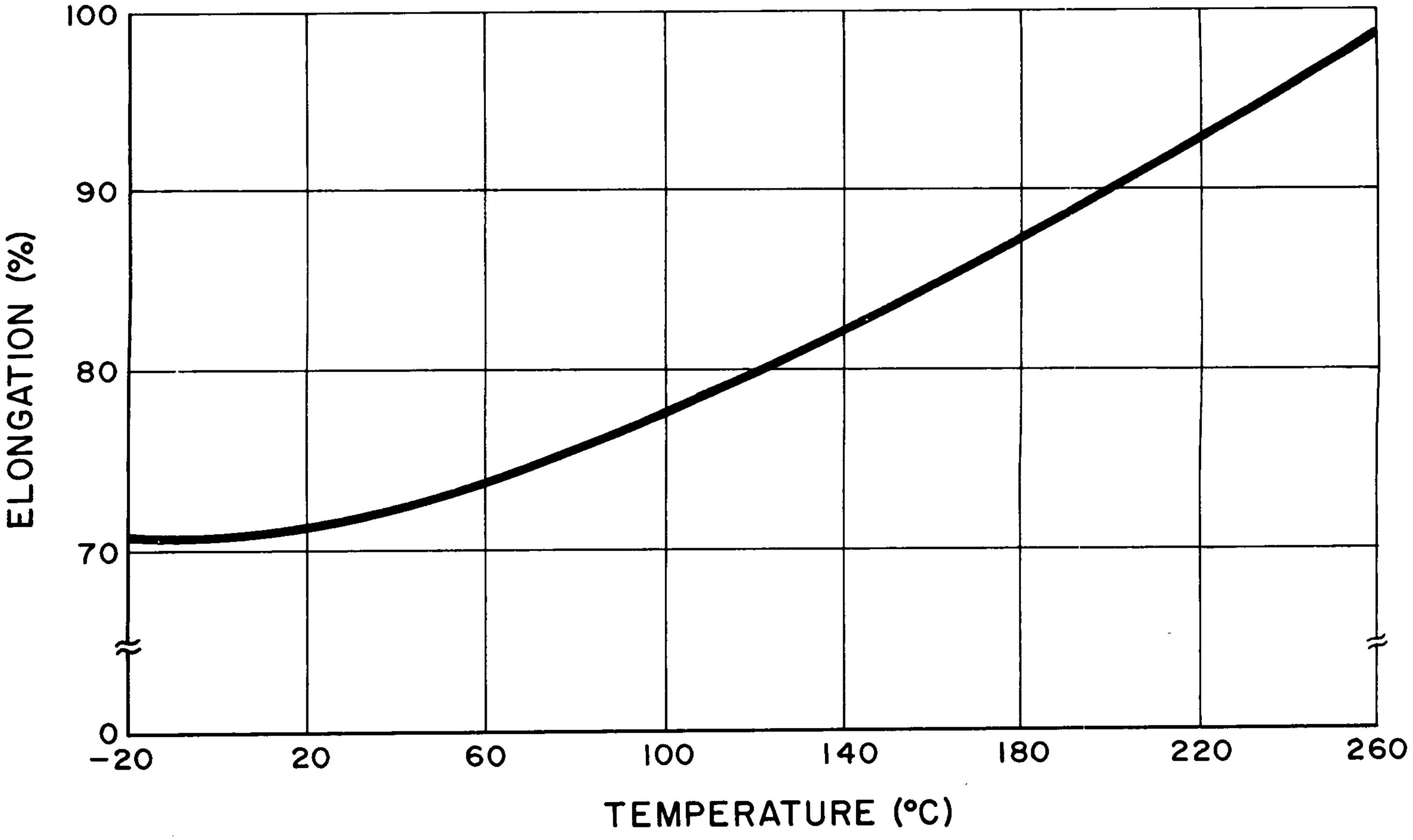


Figure 5. H-Film Elongation Versus Temperature

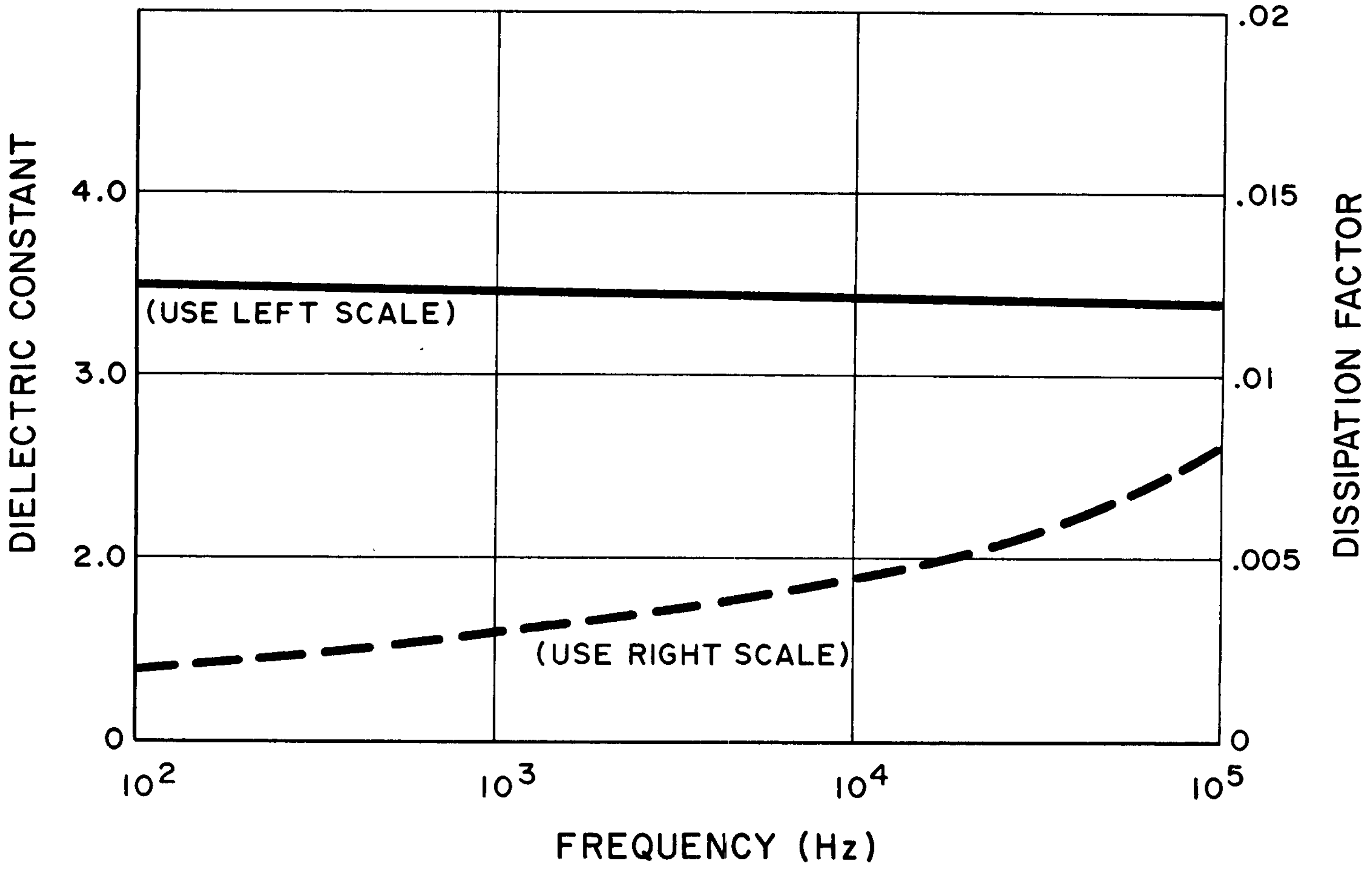


Figure 6. H-Film Dielectric Properties Versus Frequency (23 °C)

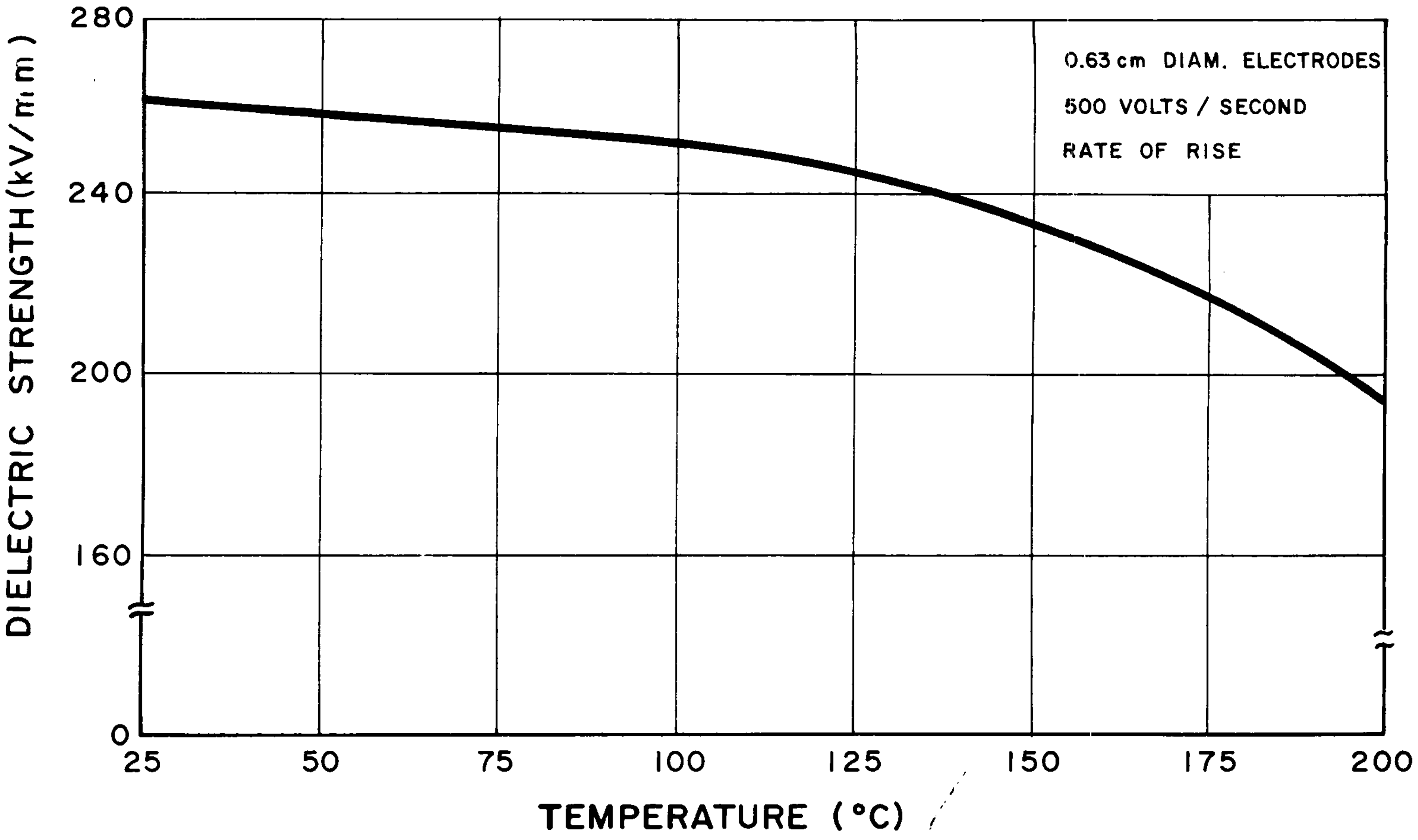


Figure 7. H-Film Dielectric Strength Versus Temperature (0.0254mm)

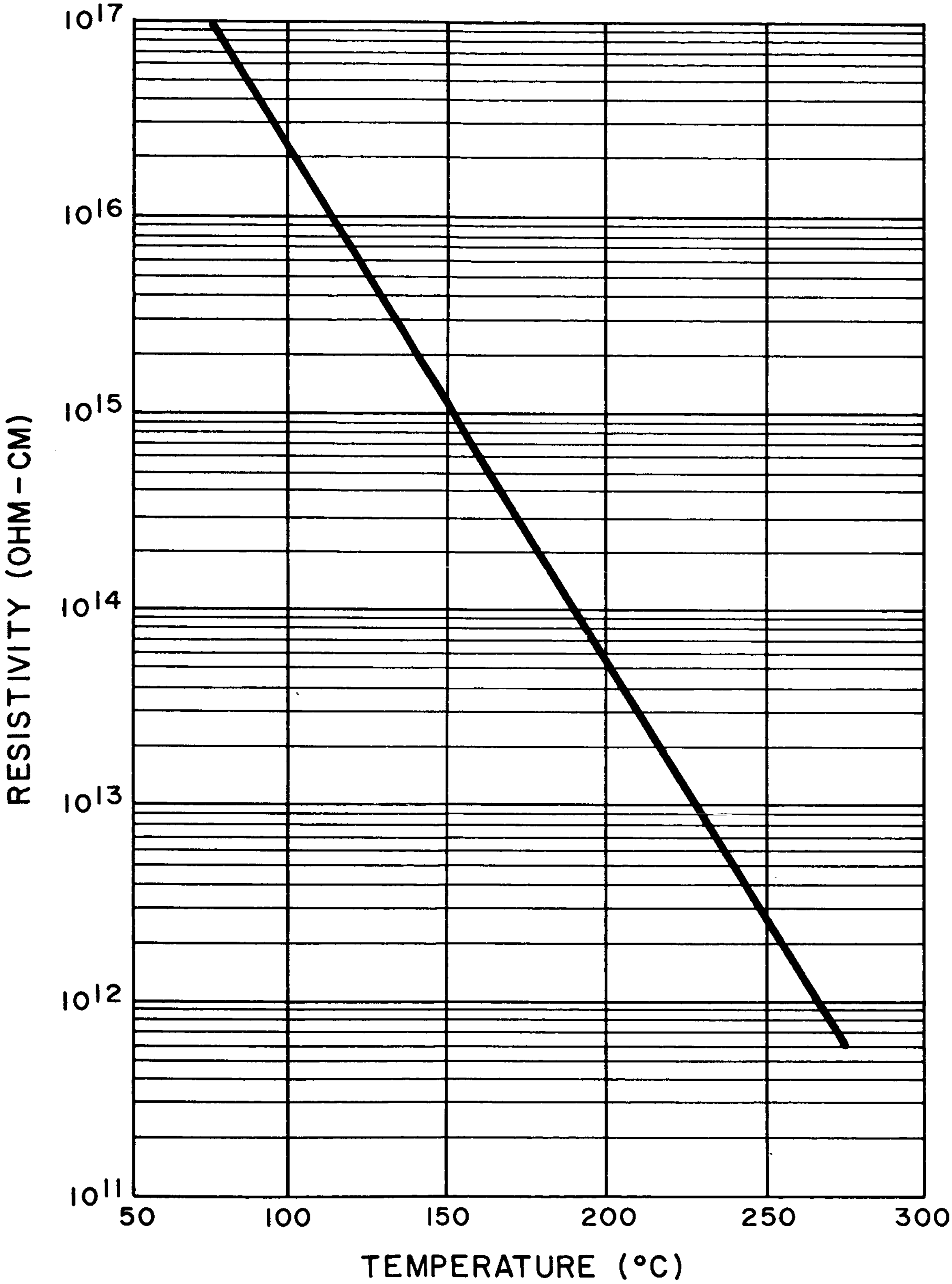


Figure 8. H-Film Resistivity Versus Temperature
(125 Volts dc)

H-Film Characteristics

Known to be radiation resistant, H-film was tested with massive radiation dosages of 2×10^6 and 2×10^7 J/kg. It was determined that the 2×10^6 J/kg radiation exposure would be sufficient to show a difference between H-film and conventional insulation. The 2×10^7 J/kg radiation exposure was planned to demonstrate some degradation of the H-film. Accordingly, at the 2×10^6 J/kg test, H-film coated with TFE*, FEP-ML**, Kynar ***, and polyethylene was compared. The results are given in Table I.

The 2×10^6 J/kg radiation exposure proved the superior radiation resistance of the H-film. For all practical purposes the H-film was unaffected; the TFE and FEP appeared to maintain their structural integrity, but the slightest bending or flexing would crack them. Kynar was nearing the end of its useful range and only by delicate handling would it take a voltage stress. The polyethylene was reduced to about one-third of its unexposed strength.

Only H-film samples were tested at the 2×10^7 J/kg radiation exposure level. The dielectric strength was tested before and after irradiation, as in the 2×10^6 J/kg test. The results are listed in Table II. An average of all samples indicated that 73 percent of the dielectric strength had been retained. As was expected, the heavier wall samples stood up somewhat better, retaining over 80 percent of their dielectric strength, while the thinner wall samples retained somewhat less than 70 percent. The all-polyimide sample (H-film cemented together with "Pyre-ML") remained unaffected by this exposure.

Cut-through measurement tests were performed to determine the electrical insulation properties of the H-film. The insulation was found to be so tough that the conductor was often damaged before the insulation was cut through. The cut-through was determined by applying a steadily increasing force to a 1.6 mm hardened steel cylindrical mandrel until it penetrated through the insulation to the conductor. To determine the point of cut-through, a buzzer was connected between the cutting mandrel and the conductor which signaled the failure of the insulation. The cut-through characteristics are given in Table III.

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* TFE - Polytetrafluoroethylene

** FEP-ML - Tetrafluoroethylene and hexafluoropropylene - polyimide

*** Kynar - Vinylidene fluoride resin

TABLE I.

DIELECTRIC STRENGTH (2 x 10^6 J/kg)

Wire Gauge	Insulation	Wall Thickness (cm)	Breakdown Voltage	
			Unirradiated	After 2 x 10^6 J/kg
24	TFE	0.010	9600	0[1]
24	Kynar	0.010	12,000	0[1,2]
24	FEP-ML	0.006	7700	0[1]
20	Polyethylene	0.064	15,000	5500
24	H-film/FEP	0.010	16,000	16,000

[1] Sample cracked on bending

[2] 10,000 volts - one sample only which was wrapped around the mandrel by slow and careful manipulation without cracking.

TABLE II.

DIELECTRIC STRENGTH (2×10^7 J/kg)

Wire Gauge	Insulation	Wall Thickness (cm)	Breakdown Voltage	
			Unirradiated	After 2×10^7 J/kg
16	H-film/FEP	0.006	5000	2000
16	H-film/FEP	0.011	11,000	6200
16	H-film/FEP	0.018	13,000	13,000
22	H-film/FEP	0.008	10,000	7850
22	H-film/FEP	0.013	14,000	9900
22	H-film/FEP	0.019	16,400	13,450
26	H-film/FEP	0.008	9800	7400
26	H-film/FEP	0.011	9900	5500
26	H-film/FEP	0.020	15,000	13,000
16	All polyimide	0.004	12,000	12,000

TABLE III.

CUT-THROUGH CHARACTERISTICS

Insulation	Type	Wall Thickness (cm)	Cut-Through (N)
TFE	ET	0.015	98
TFE	E	0.023	98
TFE	EE	0.038	160
IMP PVF[1]	2	0.043	200
Filled TFE		0.064	225
H-film/FEP	HFT	0.008	335
H-film/FEP	HF	0.011	445[2]
H-film/FEP	HHF	0.018	535[3]
TFE/Fiberglass	-	0.064	870[3]

[1] IMP PVF is irradiated modified polyolefin-irradiated polyvinylidene fluoride.

[2] Conductor generally breaks

[3] Conductor always breaks

POLYIMIDE ADHESIVES

Adhesive Requirements

Experimental polymers were tested to evaluate their potential for use as H-film adhesives. Adhesive system requirements are listed as follows:

Adherend - The adhesive will bond H-film (polyimide) to H-film and H-film to copper.

Operating Temperature - The operating temperature range will be from -65 to 300°C.

Peel Strength - The peel strength will be 2 kg/cm width minimum when pulled at an angle of 90 degrees from the adherend at a rate of 30 cm/minute through the operating temperature range.

Creep Strength - The creep strength will be 150 g/cm width minimum when pulled at an angle of 90 degrees from the adherend and will show no detectable creep or fatigue of bond after 72 hours throughout the operating temperature range.

Initial Tack - The initial tack will have a minimum of 200 g/cm width peel strength and 15 g/cm width creep strength at room temperature.

Thickness - The thickness of the adhesive will be 0.005 cm minimum and 0.008 cm maximum.

Flexibility - The adhesive will be flexible throughout the operating temperature range.

Dielectric Constant - The dielectric constant will be 4.0 maximum.

Chemical Resistance - The adhesives will be resistant to oxidation, common organic solvents and reagents, water, oils, liquid hydrogen, and liquid oxygen.

Corrosion - The adhesive will not cause corrosion to metallic parts.

Flammability - The adhesive will be self-extinguishing.

Environmental Conditions - The adhesive will retain its properties after being exposed to the following environmental conditions:

(a) Humidity - 95 percent relative humidity at 55°C for 96 hours.

(b) Fungus - In accordance with MIL-E-5272.

(c) Thermal Shock - From -65 to 300°C when tested in accordance with MIL-STD-202B.

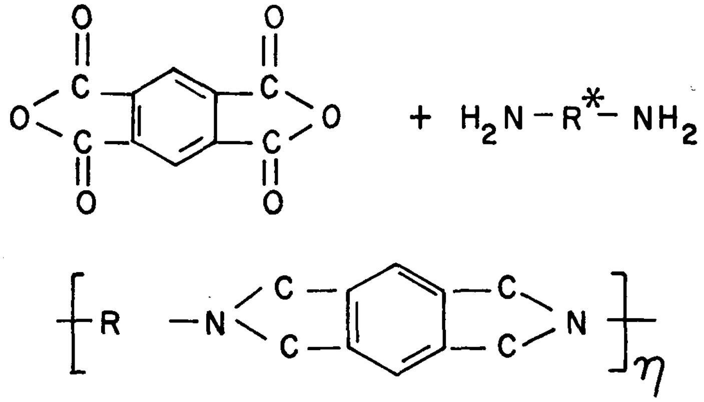
(d) Vacuum - Minimum of 1 x10^{-10} mm Hg for 10 hours at 25 ±3° C.

Aging - The adhesive will retain its properties for one year after application.

Shelf Life - The shelf life of the adhesive will be six months minimum at room temperature.

Experimental Adhesives

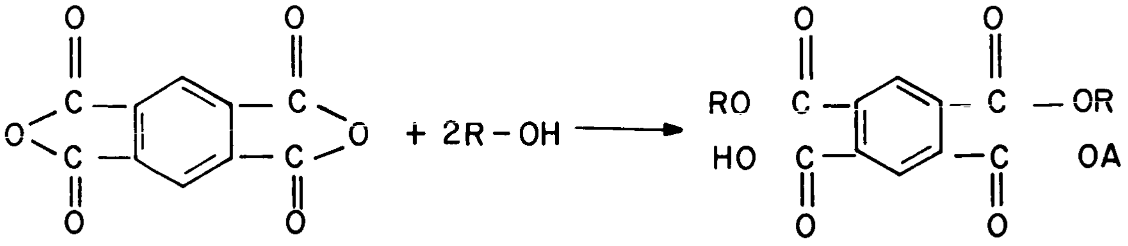
Polymers from pyromellitic dianhydride (PMDA) and aromatic or short chain diamines are highly stable and very difficult to process. The equation for PMDA is:



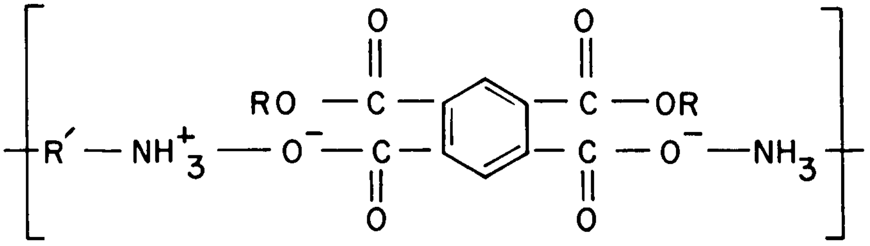
$* R = C_2$, C_6, or C_{11}

Pyromellitic Dianhydride

Diamines of different chain length were utilized to investigate the effect of chain length and to determine whether processible materials that would adhere to H-film could be obtained without sacrificing thermal stability. The Prototype Development Branch and Quantum, Incorporated,prepared all polyimides by isolating the salt of the acid and amine formed by the following general equation:

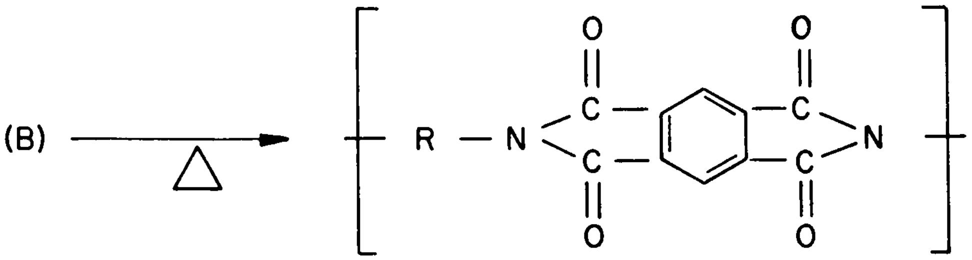


(A)



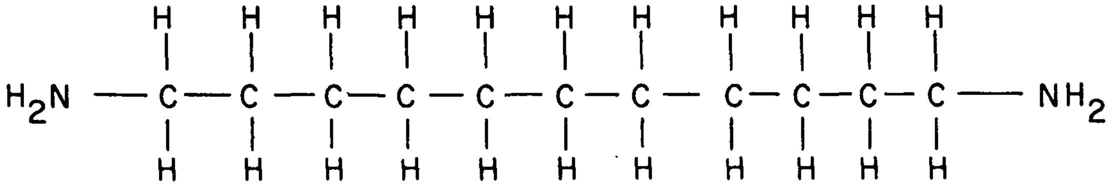
(B)

First, the half-ester of the dianhydride was prepared and reacted with a diamine. The salt produced was then processed in various ways to obtain the polyimide for particular investigations into its properties. When the salt is heated, it eliminates water and alcohol, in two steps, to form the polyimide:



PMDA was dissolved in dry methyl alcohol with slight heating to produce solution (A). This solution was cooled to room temperature; an alcohol solution of 1, 6-hexanediamine (HDA) was then added slowly while stirring the solution. A white precipitate (B) was formed immediately. The solids were then filtered and dried. The materials obtained from different polymers at this stage were usually soluble in a number of polar solvents, including water. With only slight heating they became insoluble and infusible. These factors varied from one polymer to another depending on the amine chain length and whether it contained PMDA or cyclopentane dianhydride (CPDA).

Polymers prepared with PMDA are very stable. The thermal stability is definitely related to the chain length of the diamine as the stability increases with the increase in carbon atoms in the chain. Processibility is favorably altered by an increase in chain length. The salt of PMDA and undecanediamine (UDDA) is easily processed into films, but the adhesion to H-film is not very satisfactory and the material darkens within a few minutes at temperature above 350°C. The structural formula for UDDA is:



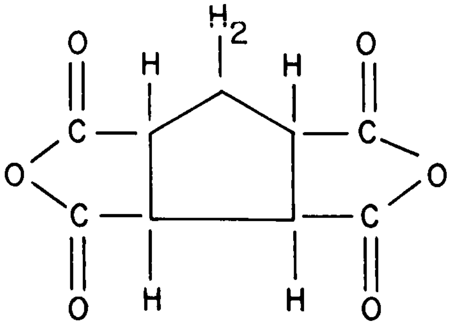
$$H_2N-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-NH_2$$

For experimental purposes, Quantum, Incorporated,prepared neocarborane from carborane by the reaction of decarborane and acetylene in the proper catalytic medium. Sublimed carborane was placed in a stainless steel pressure bomb and sealed. The bomb was then placed in a circulating oven at 500°C for a period of 20 to 24 hours. The bomb was then allowed to cool slowly and the crude product was dissolved from the walls of the bomb with ethyl ether. The ether was then evaporated and the neocarborane was sublimed at less than 1.33 N/m^2 and 100°C. A yield of approximately 85 percent with a melting point of 266°C was obtained.

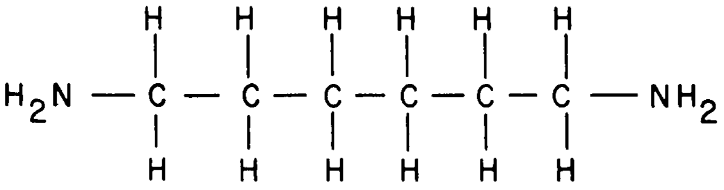
The use of carborane in polyimides will be particularly beneficial in processing the end product and for its thermal stability. The carborane groups should increase solubility in common solvents and decrease the flow point.

CPDA ADHESIVES

Experiments have been conducted on many polyimide adhesive systems, one of which is prepared from cyclopentane dianhydride (CPDA) and hexanediamine (HDA). This system is a low melting prepolymer soluble in methanol and is cured at approximately 220°C. Preliminary adhesive evaluations were made on H-film to H-film, H-film to copper, and copper to copper.



Cyclopentane Dianhydride (CPDA)



$$H_2N-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-NH_2$$

Hexanediamine (HDA)

The prepolymer was formed by first dissolving CPDA in methanol; HDA was then added with stirring. The white solids that had formed were filtered and the residue evaporated to dryness. A tacky, low-melting-temperature substance was obtained which became very hard and quite brittle when heated at 220°C for a few minutes.

Preliminary evaluations of the stability of cured samples of H-film laminated to H-film were conducted at temperature ranges from 320 to 430°C for one hour periods. Two methods of testing were used; (1) samples were clamped between steel plates, and (2) samples were set loose in the oven. Samples tested by the two methods were inspected after the heat treatment and the results are listed in Table IV.

TABLE IV.

H-FILM LAMINATED TO H-FILM

Samples	Characteristics		
	at 320°C	at 380°C	at 430°C
Clamped	good adhesion	good adhesion	fair adhesion
Loose	good adhesion	slight bubbling, fair adhesion	considerable bubbling, poor adhesion

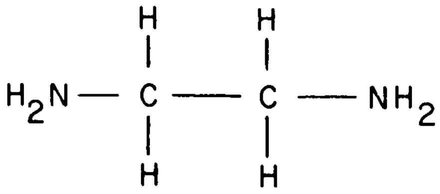
Several new types of experimental syntheses of the CPDA material have been produced. The most promising of these are given in Table V.

TABLE V.

CPDA EXPERIMENTAL SYNTHESES

CPDA	42.0 g	CPDA	42.0 g
HDA	22.5 g	Phthalic acid	3.3 g
Methanol	solvent	Oxydianiline	16.0 g
N, N - Dimethylacetamide	solvent	N, N - Dimethylacetamide	solvent
CPDA	42.0 g	CPDA	16.8 g
Terephthalic acid	3.3 g	Terephthalic acid	3.3 g
Oxydianiline	16.0 g	HDA	23.2 g
N, N - Dimethylacetamide	solvent	N, N - Dimethylacetamide	solvent

A typical preparation follows. CPDA (16.8 g) was charged into a three-neck, round bottom flask containing 150 milliliters of N, N-dimethylacetamide and fitted with a stirrer and reflux condenser. Tetrephthalic acid (3.3 g) was added to the mixture, which was stirred until all solids were dissolved. HDA (23.7 g) in an N, N-dimethylacetamide solution was then slowly added. The resulting exothermic reaction temperature was controlled with cooling below 60°C. This mixture was then stirred and heated at reflux for two hours. CPDA/ETDA has also yielded promising results:



$$H_2N - \overset{H}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - NH_2$$

1, 2 - Ethylenediamine (ETDA)

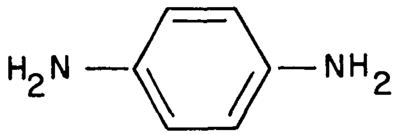
The following is the general procedure used in preparing various polymers. The anhydride was charged into a reaction flask containing a high excess of methanol and dissolved by heating. A methanol solution of the amine was then slowly added to the flask while stirring. After heating at reflux for one-half hour, the solution was rotated until a solid was formed. Some polymer formulations are listed in Table VI.

TABLE VI.

POLYMER FORMULATIONS

I-23	I-24	I-25	I-26	I-27
CPDA 21.0 g M-PDA 10.8 g MeOH excess	CPDA 21.0 g P-PDA 5.4 g MeOH excess	CPDA 10.5 g ETDA 3.0 g MeOH excess	CPDA 10.5 g P-PDA 2.7 g H-DA 3.0 g MeOH excess	CPDA 10.5 g O-PDA 5.4 g MeOH excess

Adhesion tests were made on H-film to H-film, H-film to copper, and copper to copper laminations by coating the laminating surfaces and pressing them together between metal plates. They were then cured for 10 to 15 minutes at a temperature between 300 and 380°C. The PDA materials did not show promise of good adhesion. The ETDA materials appeared to have better adhesive qualities than the HDA materials. The adhesion of both materials was greater than the tear strength of the H-film since laminates were inseparable without tearing.



Para Phenylenediamine (P-PDA)

The useful materials (ETDA and HDA resins) were evaluated at 300°C, 400°C, and 500°C. The first noticeable adverse effect was blackening of the adhesive. After 30 minutes at 300°C, good adhesion remained but blackening around the edges of the samples occurred. After 30 minutes at 400°C, some adhesion remained and the adhesive turned very dark. After 10 minutes at 500°C, only slight adhesion remained in spots and the adhesive turned black.

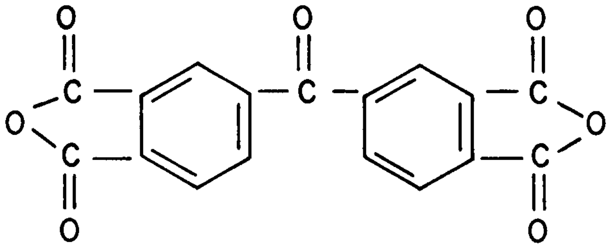
CPDA/ETDA adhesive is more effective in laminating H-film and copper than the CPDA/HDA polymer. Although these materials are more brittle than is desirable, it is believed that this can be reduced by incorporating higher chain length diamines, plasticizing with silicones, and preparing resins with a mixture of diamines of varying chain lengths.

BTDA ADHESIVES

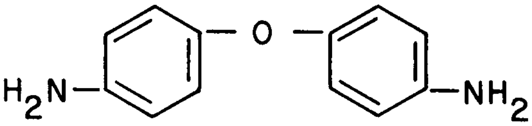
Many polyimide systems have been prepared and screened. The most promising systems have been established as those derived from BTDA and various diamines. This was determined from the standpoint of the most satisfactory combination of properties.

Those systems containing aliphatic diamines exhibit desirable physical properties and processibility, but are poor in thermal stability. Those systems containing aromatic diamines exhibit good thermal stability and can be processed from solutions and powders, although not as readily as the aliphatic derivatives. The aromatics also exhibit good physical properties, although not as good as the aliphatics. These properties of aromatic versus aliphatic systems follow the expected pattern, after consideration of the molecular structures.

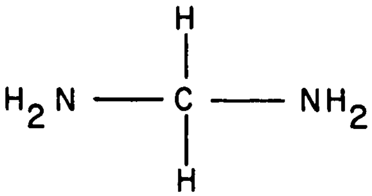
Materials prepared from BTDA and ODA may be deposited from solution as a salt or molded as a powder. The thermal stability appears to be similar to that of H-film, decomposing within 20 hours at 400°C with relatively small weight losses at 300°C during the same period.



Benzophenonetetracarboxylicdianhydride (BTDA)

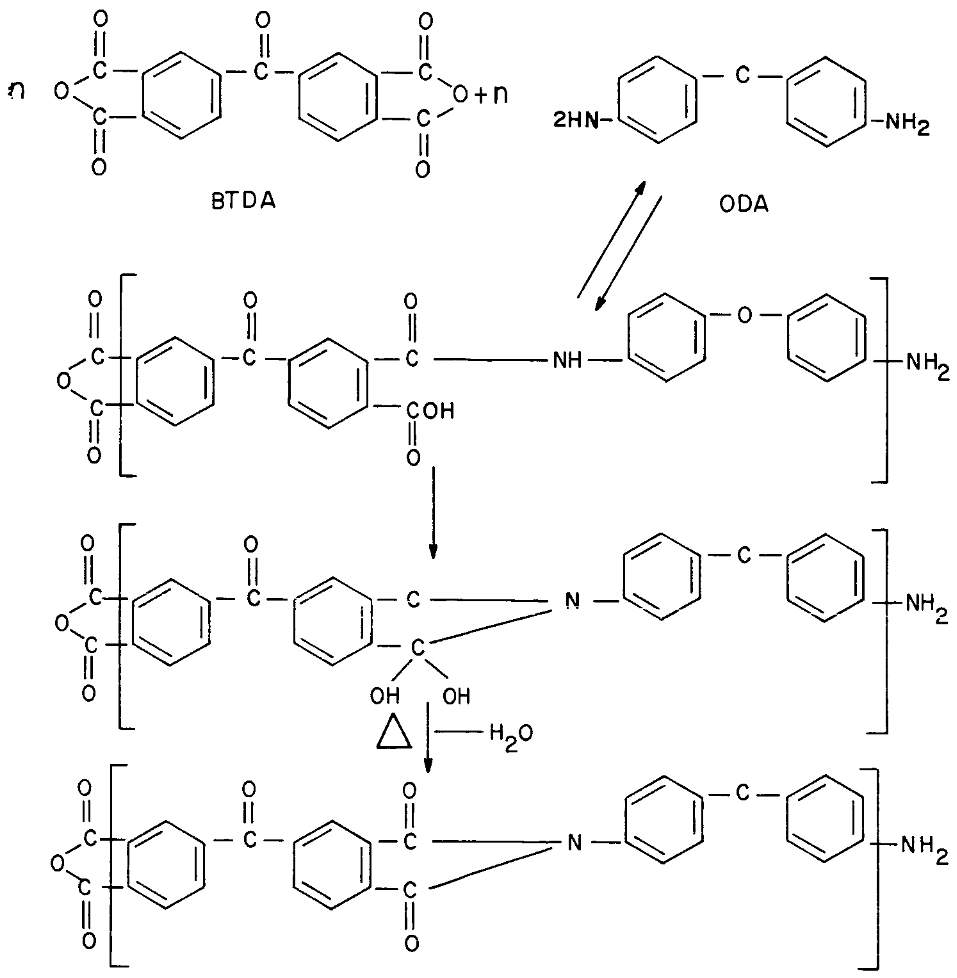


Oxydianiline (ODA)



Methylenedianiline (MDA)

The BTDA-ODA polyimide reaction sequence is shown as follows:



BTDA-ODA Polyimide Reaction Sequence

Adhesion of the BTDA-ODA resin was tested by evaluating tensile shear and peel strength of laminated H-film, copper, and steel. Some of the results are as follows:

(1) H-film laminated to H-film with BTDA, HDA, ODA, and MDA, with a 1.27 cm overlap of the laminate, broke in all cases at the H-film with no separation of the laminate. The calculated tensile shear at break was 2.48 x 10^8 to 3.10 x 10^8 N/m^2.

(2) Copper laminated to copper with BTDA-ODA resin. The calculated tensile shear strengths for various tests were 165×10^4, 178×10^4, 192×10^4, and 178×10^4 N/m^2. These values are considered low because distortion of the 0.0762 mm copper under test caused delamination by forces other than shear.

(3) Steel laminated to steel with BTDA-ODA resin. The calculated tensile strengths were 118×10^5, 138×10^5, 144×10^5, and 124×10^5 N/m^2.

Typical peel strength values for H-film to H-film and H-film to copper are 1760, 2800, 1575, and 3150 N/m. These values do not indicate true peel values as all samples tore at the H-film; consequently, true adhesion values could not be obtained. This was true for all resins investigated.

Emphasis has been placed upon the evaluation of the BTDA-ODA material because it appears to offer the most promise as an H-film adhesive and exhibits good thermal stability.

Experiments have been conducted with several materials to find a polyimide with satisfactory physical properties. Experimental preparations are given in Table VII.

TABLE VII.

BTDA EXPERIMENTAL SYNTHESES

BTDA (half-ester)	19.3 g	BTDA (half-ester)	19.3 g
M-PDA	5.4 g	ODA	10.0 g
Bis (2-ethoxyethyl) Ether	solvent	Bis (2-ethoxyethyl) Ether	solvent

BTDA	32.2 g	BTDA	32.2 g	BTDA	32.3 g
ETDA	19.8 g	HDA	11.6 g	ODA	20.0 g
Methanol	solvent	Methanol	solvent	Methanol	solvent

A typical procedure involving a BTDA/ODA preparation follows. A three-neck, 500-milliliter round bottom flask was fitted with a thermometer, stirrer, and reflux condensers. The flask was then charged with BTDA and excess methanol. The BTDA/MeOH* mixture was then stirred and heated until a clear solution resulted. The solution was then cooled to room temperature and ODA, dispersed in methanol, was added slowly. A slight exotherm occurred and the solution became clear within several minutes after heat was reapplied. Stirring at reflux (65°C) was continued for one hour and the solvent was then evaporated under reduced pressure. The crystalline solids thus obtained were stored in a closed glass container.

The evaluations and determinations of the physical properties of various BTDA polyimide systems are given in Tables VIII, IX, and X.

TABLE VIII.

H-FILM TO H-FILM PEEL STRENGTH

Samples**	Peel Strength N/m width	
	At 25°C	After 30 minutes at 400°C
1	870	700
2	700	790
3	790	870
Average	786	786

** All samples broke at the H-film without delaminating.

The preparations which offer the most promise as polyimide adhesive of the experimental syntheses attempted are given in Table IX.

The first two preparations (Table XI) consisted of making the half-ester in methanol and then carrying out the reaction to the polyimide in N, N-dimethylacetamide. The last of the preparations involved a method whereby the soluble polyimide was synthesized in N, N-dimethylacetamide without first forming the half-ester. The polyimide was then converted to the insoluble polyimide by heating. N, N-dimethylacetamide has been found to be more suited to these preparations than other solvents because of the greater solubility and the fact

---

* Methanol

TABLE IX.

THERMAL STABILITY OF VARIOUS POLYMERS

Polymers	Time tested (hours)	Weight Loss (percent) (cured samples)
BTDA/ODA	22	4 (300°C)
BTDA/MDA	15	3 (300°C)
BTDA/ODA	6	18 (400°C)
BTDA/ODA	28	100 (400°C)
BTDA/P-PDA	19	100 (400°C)
H-film *	19	100 (400°C)

* The H-film decomposed completely after 19 hours, showing that BTDA/ODA polymer is more stable than the H-film.

TABLE X.

TENSILE STRENGTH OF VARIOUS POLYMERS

Polymers	Tensile Strength (N/m^2)
BTDA/PDA	248×10^5
BTDA/HDA	340×10^5
BTDA/MDA	750×10^5
BTDA/ODA	235×10^5

that better films, which are necessary in processing laminates of H-film, can be obtained. Preparations 1 and 2 (with half-ester conversions) and Preparation 3 (the direct anhydride amination) have shown good characteristics.

(1) The polymer obtained by way of the half-ester appears to have a more linear structure in that it has better flow properties in the cured form than the direct anhydride amination and is feasible as would be expected.

TABLE XI.

BTDA EXPERIMENTAL PREPARATIONS

Preparation 1		Preparation 2		Preparation 3	
BTDA	32.2 g	BTDA	64.4 g	BTDA	32.2 g
ODA	20.0 g	HDA	23.2 g	ODA	20.0 g
Methanol	solvent	Methanol	solvent	N, N-dimethyl-acetamide	solvent
N, N-dimethyl-acetamide	solvent	N, N-dimethyl-acetamide	solvent		

(2) The polymer prepared directly from the anhydride (BTDA) and amine can be deposited as a film more readily than Preparation 1, but is not feasible because it should be crosslinked to a greater extent.

These materials showed good adhesion to H-film and copper; however, bubbles formed between the laminate during cure and created problems. Electrical tests were conducted on polyimides prepared in various convenient forms and have shown good results. Some dielectric breakdown results are shown in Table XII.

TABLE XII.

POLYIMIDE DIELECTRIC BREAKDOWN

Material	Thickness (cm)	Breakdown Voltage (volts)	Dielectric Strength (volts/mm)
BTDA ODA Dimethylacetamide	0.006 0.003 0.003	3800 3000 1500	60,000 118,000 59,000
BTDA/MDA	0.003	7500	196,000
BTDA UDDA MeOH Bis (2-ethoxyethyl) - ether	0.004	5300	116,000
Laminated H-film	0.022	12,500	57,000

The electrical properties and thermal stability of the materials listed in Table XII are comparable to such dielectrics as H-film and Teflon. Polyimides prepared from BTDA/ODA were compared in simultaneous tests under identical test conditions. These polyimides were shown to be comparable to H-film and Teflon. At 400°C, it was found that Teflon loses weight at a greater rate than the polyimides (Fig. 9) and its total decomposition occurs before the polyimides. Some typical values obtained from BTDA polyimides prepared in various forms are shown in Table XIII.

TABLE XIII.

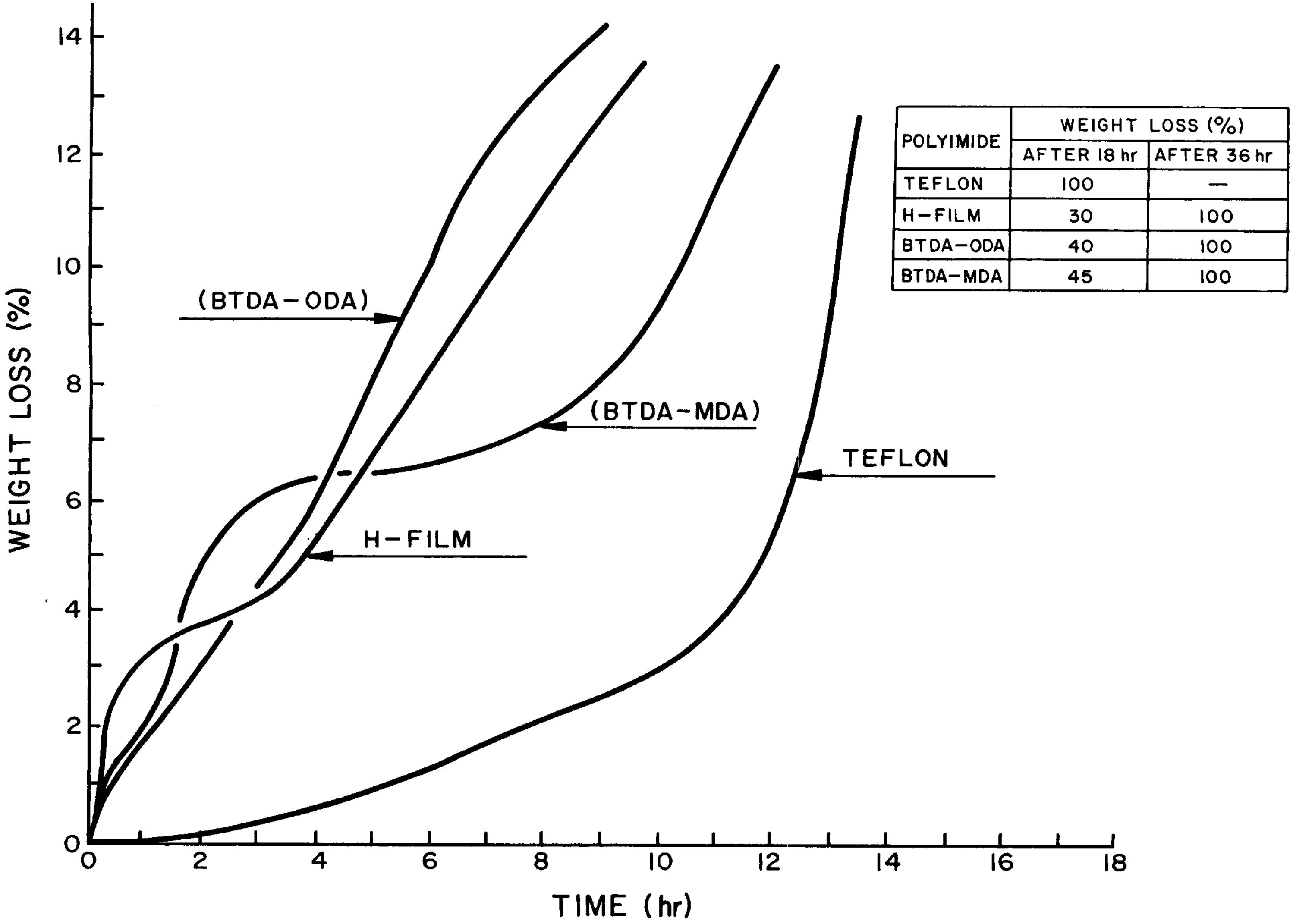
BTDA POLYIMIDE ELECTRICAL CHARACTERISTICS

Material	Sample Thickness (cm)	Dielectric Constant	Dissipation* Factor
BTDA/MDA	0.152	3.54	<0.001
BTDA/ODA	0.254	3.79	<0.001
BTDA, HDA, MeOH, N, N-dimethylacetamide	0.399	4.71	<0.001

* All values were less than the minimum bridge capacity of 0.1 percent.

A typical procedure for the preparation of a BTDA/ODA polyimide in N, N-dimethylacetamide follows. A three-neck, 500-milliliter round bottom flask was filled with a stirrer, thermometer, and reflux condenser. The flask was then charged with BTDA and N, N-dimethylacetamide. Stirring and heating were applied until BTDA dissolved. The temperature of the solution was cooled to 60°C and then ODA dissolved in N, N-dimethylacetamide was added slowly. A slight exotherm occurred, but the solution remained clear. Stirring at reflux was continued for two hours. During this time, a fine yellow precipitate occurred. The solids were filtered off and washed in acetone.

Some improvement in processing was obtained by the direct amination of BTDA with various diamines in N, N-dimethylacetamide solvent because of increased solubility and easier film preparation.



POLYIMIDE	WEIGHT LOSS (%)	
	AFTER 18 hr	AFTER 36 hr
TEFLON	100	—
H-FILM	30	100
BTDA-ODA	40	100
BTDA-MDA	45	100

Figure 9. Thermal Stability Comparison at 400°C

Chemical resistance to chemical reagents of three polyimides was tested in accordance with ASTM Specification D543-60T at room temperature. Specimens consisted of 2.54 x 5.08 x 1.27 cm molded polyimide strips. Weight and thickness changes over a seven-day period were recorded for two samples of each polyimide in each reagent involved. The specimens were weighed before and after immersion on an analytical balance and thickness changes were determined using a Hanson micrometer. The test results are shown in Table XIV. All polyimides tested were attacked mostly by strong bases and strong acids. Strong bases attack these materials by saponification.

TABLE XIV.

POLYIMIDE CHEMICAL RESISTANCE CHARACTERISTICS

Reagent	Polyimide Type	Weight Change (percent)	Thickness Change (percent)
Acetone	ODA	0.02	0.39
		0.05	3.95
	HDA	0.03	0.59
		0.04	0.62
	MDA	0.47	--
		0.37	--
HC1 (conc)	ODA	0.29	--
		0.28	--
	HDA	0.72	--
		0.43	0.25
	MDA	0.54	--
		0.45	--
Iso-octane	ODA	0.11	--
		0.15	--
	HDA	0.03	--
		0.08	--
	MDA	0.14	--
		0.03	--
Stoddard Solvent	ODA	0.11	--
		0.10	--
	HDA	0.20	--
		0.14	--
	MDA	--	--
		0.05	--

TABLE XIV.

POLYIMIDE CHEMICAL RESISTANCE CHARACTERISTICS (Cont'd)

Reagent	Polyimide Type	Weight Change (percent)	Thickness Change (percent)
Mineral Oil (Marcol)	ODA	0.22	--
		0.23	--
	HDA	0.01	--
		0.10	--
	MDA	0.25	--
		0.31	--
HNO_3 (40 percent)	ODA	1.22	--
		1.38	0.53
	HDA	1.26	--
		1.30	--
	MDA	0.85	1.14
		0.95	0.79
Benzene	ODA	0.49	--
		0.09	--
	HDA	0.04	--
		0.07	--
	MDA	--	--
		0.06	--
CCl_4	ODA	0.06	--
		0.10	--
	HDA	0.03	--
		0.01	--
	MDA	0.13	--
		0.11	--
H_2O	ODA	0.53	--
		0.42	--
	HDA	0.32	--
		0.31	--
	MDA	0.90	--
		0.95	--

TABLE XIV.

POLYIMIDE CHEMICAL RESISTANCE CHARACTERISTICS (Cont'd)

Reagent	Polyimide Type	Weight Change (percent)	Thickness Change (percent)
NaOH (10 percent)	ODA	1.66	0.72
		1.40	1.46
	HDA	0.68	0.42
		0.58	0.29
	MDA	5.05	1.06
		4.71	7.21
H_2SO_4 (30 percent)	ODA	0.61	--
		0.88	--
	HDA	0.28	--
		0.35	--
	MDA	1.01	--
		0.97	--

The flammability of four different polyimides was tested. The materials and compositions of these polyimides are given in Table XV.

TABLE XV.

POLYIMIDE COMPOSITIONS

I-73	I-80	I-81	I-86
BTDA	BTDA	BTDA	BTDA
HDA	ODA	MDA	ODA

Three molded specimens (12.7 cm long, 1.27 cm wide, and at least 0.127 cm thick) of each polyimide (Table XV) were tested. The sample was clamped in a support so that its longitudinal axis was horizontal and its transverse axis was inclined 45 degrees horizontally. A propane torch was used in attempting to ignite the specimen. The tip of the flame was allowed to contact the end of the sample for 30 seconds and then removed.

After two attempts, the sample was determined to be noncombustible if it did not ignite. Results indicated that these polyimides do not support combustion.

B-STAGE ADHESIVES

The best method of preparing H-film for lamination is to coat BTDA/ODA polyimide on one side of the H-film by brushing and curing the polyimide adhesive to an advanced B-stage. An advanced B-stage is reached by maintaining the temperature of the polyimide at approximately 150°C for more than one hour after allowing adequate drying at a lower temperature. The BTDA/ODA system was chosen as it best meets the requirements of stability and processibility. Because of its chemical structure, processing is easier than that for PMDA systems, but the BTDA system is still only processible to a certain point in its curing stage. This curing stage allows a minimum of gas to evolve and still maintains enough flow to allow adhesion to the surfaces being laminated. Considerable difficulty has been experienced in obtaining smooth coated film because of shrinkage of the coating during curing. A degree of success has been achieved by maintaining the H-film spiraled around a cylindrical mandrel before coating and during the B-stage cycling. This technique keeps shrinkage deformation of the substrate at a minimum.

The B-stage cycling for the resin is dependent upon the thickness of a particular structure. Normally, where 0.005 cm or less of resin is used, it is expected that the solvent will be evaporated at a temperature between 90 and 100°C for approximately one hour and then cured at a temperature of approximately 200°C for one-half hour. The resulting resin may then be used in laminating; either a press at 370° C or rollers at 425°C may be used.

The following new method of preparation provides improved workability to the casting of B-stage polyimide films.

A three-neck, 500-milliliter round bottom flask was fitted with a stirrer and a thermometer. The flask was charged with approximately 100 milliliters of N, N-dimethylacetamide. A thoroughly mixed blend of 64.4 grams of BTDA and 39.6 grams of MDA was then added to the flask while stirring. The resulting exotherm was controlled below 50° C using wet ice. With the completion of the addition of the dry powder mixture, the solution was stirred until the exothermic reaction was complete.

Excellent films, both flexible and tough, were obtained from the preparation made in this manner. The films were prepared by casting the B-stage solution upon a glass plate, drying slowly at 90° C, and then stripping the clear, flexible film from the glass. Some of the films were converted to the polyimide by heating at 170°C for an extended period. These investigations were conducted in an effort to work out a process for preparing H-film laminates.

A general description of the experimental rollers constructed for laminating H-film is discussed in the following paragraph.

Two 7.62-cm diameter by 15.24-cm length stainless steel rollers are mounted in a frame so that adjustments of thickness and pressure can be made manually on each side of the rollers. Each roller is attached to a gear that meshes with the other. A 1.27-cm diameter by 15.24-cm length heater is inserted into the center of each roller. The rollers are heated during operation through a brush and ring arrangement. Current input is controlled by a variable transformer, permitting temperature control within adequate tolerances. Materials to be laminated are passed through the rollers while they are rotating. Adequate speed rates are difficult since the rotation cannot be precisely controlled. Although limited areas of good lamination are obtained, problems continue to be encountered in forming a continuous homogeneous laminate, primarily because of gas formation and shrinkage.

MOLDING COMPOUNDS

Polyimide materials and other plastics may be obtained in molding compounds which are used in transfer and compression molding presses. The molding compound is a fast curing compound with extremely soft flow and long flow time. The material should be granular and preformable; it should have six months shelf life without refrigeration and should not be affected by solvents, weak alkalies, and weak acids. The compound is used for sealing and encapsulating electrical parts, such as plugs and receptacles (for flat conductor cables), and electronic components. The specifications for transfer molding compounds used for such purposes are given in Table XVI.

TABLE XVI.

MOLDING COMPOUND SPECIFICATIONS

Property	Specification
Molding	
Bulk factor	2 - 4
Plasticity	Extremely soft
Spiral flow (3.45×10^6 N/m^2, 150°C)	1.016 m
Transfer molding pressure	1.72×10^5 to 5.16×10^5 N/m^2
Molding temperature	110 to 140°C
Cure time .152 cm	2 min
Shelf stability of 21°C	6 months
Cured	
Flexural strength	6.90×10^7 N/m^2
Heat resistance, continuous	135°C min.
Flame resistance	self-extinguishing
Molding shrinkage cm/cm	0.003 or less
Total shrinkage after full cure cm/cm	0.005 or less

CONCLUSIONS

H-film polyimide is a new material possessing high temperature stability, low temperature flexibility, high radiation resistance, and high dielectric strength. It can be used in many phases of the electronics field.

Of the many adhesive systems under experimentation, the system derived from BTDA appears to be most promising. This system exhibits good physical properties, processibility, and thermal stability. The thermal stability is similar to that of H-film. The electrical properties exhibited are very satisfactory. The dielectric breakdown voltage is above 5900 volts/cm (not as high as H-film but sufficient), the dielectric constant is less than 4.0, and the dissipation factor is less than 0.1 percent.

Good adhesion to the H-film has been obtained; however, laminating the H-film without getting bubbles is a problem. It is believed that satisfactory laminations can be prepared to demonstrate the feasibility of hot rollers once the related conditions have been established. This work should lead to relatively easy development of a process where adequate equipment is available.

Several other types of polyimide materials are available from the following companies: Westinghouse Electric Corporation, Amoco Incorporated, and American Cyanamid Corporation. All these materials are different in structure from the previously discussed du Pont material and BTDA-ODA material; BTDA-ODA material was developed under contract for MSFC-NASA.

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APPROVAL

HIGH TEMPERATURE POLYIMIDES FOR ELECTRICAL EQUIPMENT

By Bobby W. Kennedy

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This report has also been reviewed and approved for technical accuracy.

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