EMPLOYMENT OF METAL-MODIFIED POLYIMIDE TO ACHIEVE OPTIMUM CONDUCTANCE AT AN ALUMINUM JOINT

by

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This thesis is dedicated to

Robert J. Calvey

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TABLE OF CONTENTS

Page

LIST OF FIGURES

Figure		Page

LIST OF TABLES

I. INTRODUCTION

Polymeric materials which have been developed for their thermal oxidative stability include: polybenzimidazoles, poly(phenylquinoxalines), polyimides and polyamides.[1] Within the class of thermally stable polymers, the aromatic polyimides have become the standard of reference for high temperature performance.[2]

Polyimides are usually derived from aromatic diamines and tetracarboxylic acid dianhydrides. Some of the general properties of aromatic polyimides discussed by Cassidy[3] follow. Polyimides have excellent thermal stability in air at temperatures between 275-300°C by isothermal testing methods. Their glass transition temperature ranges between 280-385°C depending on the method used in its determination. Polyimides are good insulators with low dielectric constants ranging between 2.8 and 3.2 at 200°C. Also, the color of polyimides vary between colorless to deep red depending on the diamine used.

Polyimides have been employed as precured films, fibers, curable enamels, adhesive and composite resins.[1] Research relating to the use of polyimides modified with metal-ion complexes and metal particles indicate that enhanced conductivity[4-13] and adhesive strength[14-17] can be achieved.

The objective of this research was to study the feasibility of using metal-modified polyimides in a novel application. The application has been proposed by the Aluminum Company of America (Alcoa). The goal is to maximize electrical joint stability at optimum conductance by using a

polymer matrix doped with a variety of metal-ion complexes or metal particles. Since the temperature of the electrical joint can reach approximately 200°C in use, polyimides have been chosen as the polymer matrix.

The following thesis briefly reviews the literature dealing with polyimides and discusses the research effort relating to the feasibility study of the above application.

II. HISTORICAL

The following chapter is a brief review of the literature related to polyimides, modification of polymides and metal-polymer adhesion, specifically aluminum-polyimide adhesion. This review is not meant to be exhaustive, but instead an introduction to the available literature.

A. Condensation Polyimides

Aromatic polyimides are noted for their thermal stability, resistance to irradiation, mechanical deformation at high temperatures and inertness to solvent attack.[2] These materials are usually synthesized by a two step process where initially a soluble poly(amic acid) is prepared by the reaction of an aromatic diamine and an aromatic dianhydride in an aprotic solvent such as dimethylacetamide (DMAC). Imidization is then achieved by either thermal or chemical cyclization (Figure 1). One method[2] of thermal imidization involves partial drying of the poly(amic acid) film to a solids content of 65-75% followed by gradual heating to 300°C and then maintenance of this temperature for an hour. Chemical imidization involves the use of a basic catalyst, such as pyridine, and a dehydrating agent, such as, acetic anhydride,[2] usually at room temperature. Polyimides, thus prepared, are conventionally referred to as condensation polyimides due to the elimination of water in the imidization step.

Condensation polyimides are found to be thermally stable. As previously mentioned, the thermal stability in air of polyimides is reported to be between 275°C and 300°C by isothermal methods.[3] The

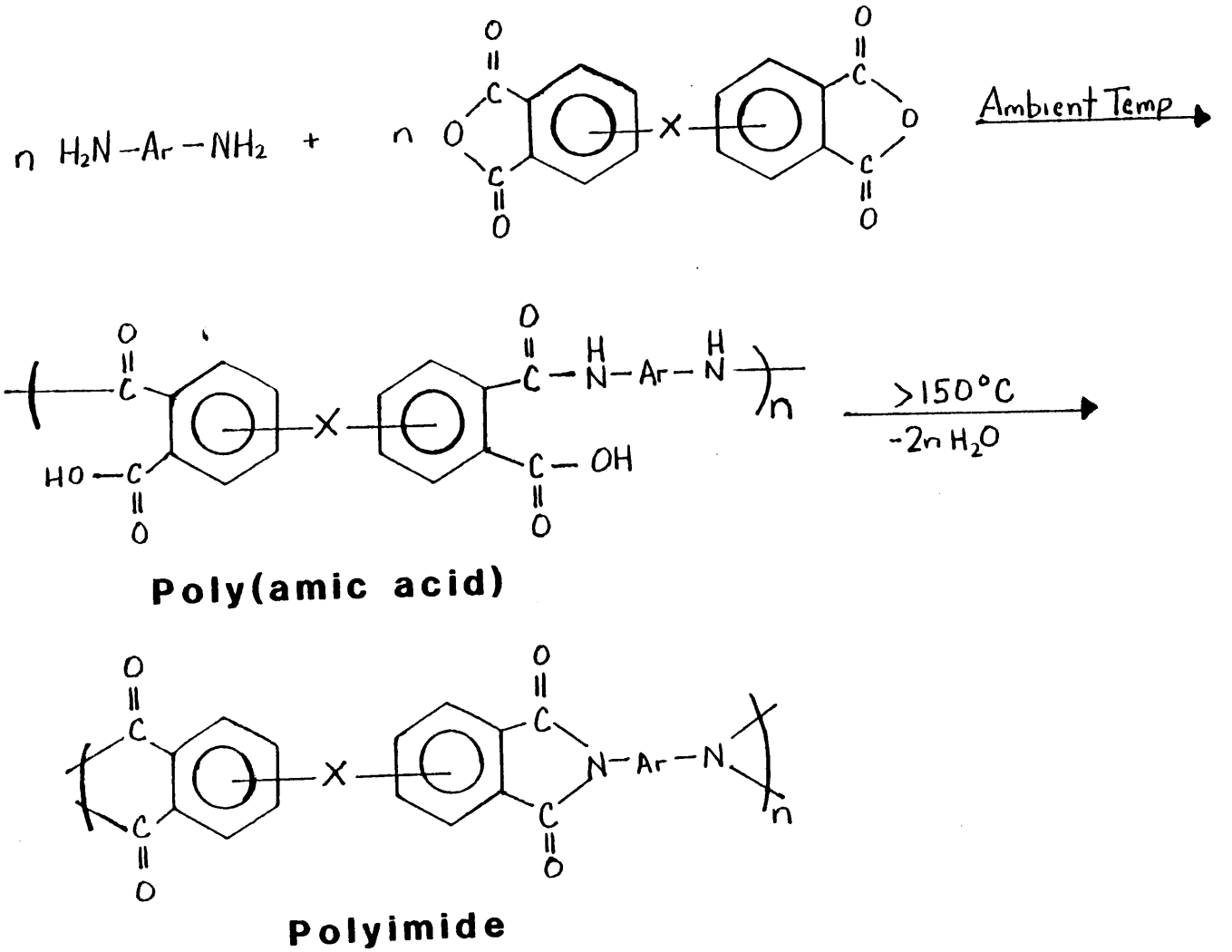

Figure 1. Conventional Polyimide Synthetic Route

recurring units in the imide backbone have a pronounced effect on the thermal stability. Reddy[18] lists the order of thermal stabilities of various diamines and dianhydrides. In general, aromatic moieties are more thermally stable than aliphatic moieties (Figure 2). The position of the recurring unit relative to the imide moiety also has an effect on the thermal properties of polyimides. Para catenation gives higher decomposition temperatures than meta catenation. It also should be noted that as the thermal stability decreases, the polyimides become more soluble and easier to process.

Polyimides are soluble in solvents such as concentrated sulfuric acid and/or fuming nitric acid. Ryntz[19] suggests that insolubility in conventional solvents is not inherent in the backbone structure but is due to apparent crosslinking that often occurs during the dehydration of the poly(amic acid) precursor. Alternative methods of incorporating the imide backbone into a polymer system, to increase solubiliity, have been employed. One method involves synthesizing aromatic polyimides via a Diels-Alder reaction[19,20] (Figure 3). With this method the imide moiety is pre-formed in the monomer, thus preventing any crosslinking due to the dehydration of the amic acid intermediate in the conventional synthesis. Another means to increase solubility is to introduce pendent phenyl groups along the polyimide backbone.[21] Polyimides synthesized via these methods are found to be soluble in chlorinated hydrocarbons, such as, chloroform.

The insolubility of polyimides in conventional solvents leads to difficulties in the fabrication of these compounds and therefore,

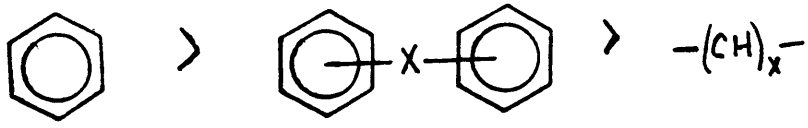

Figure 2. General Order of Thermal Stabilities of Recurring Units in the Polyimide Backbone

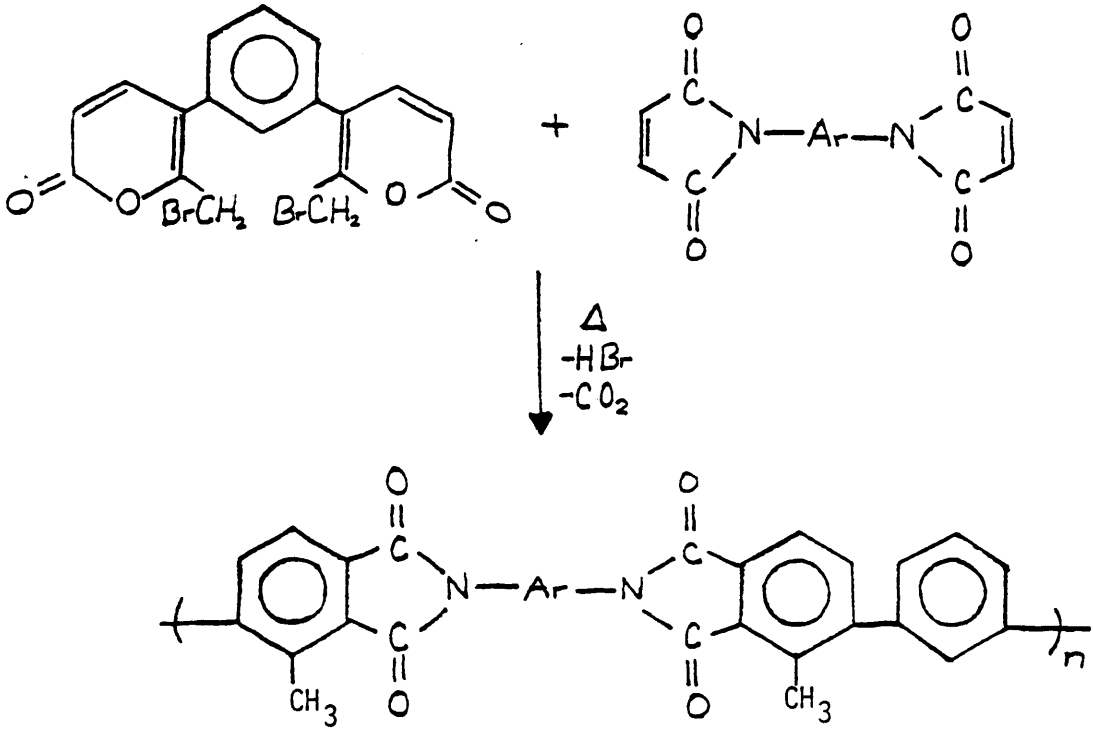

Figure 3. Diels-Alder Synthetic Route (Ref. 19)

materials are usually processed at the poly(amic acid) stage. Due to the release of water during the imidization step, the use of polyimides processed at the poly(amic acid) stage, in void-free applications is limited. An example of such an application would be using polyimides as adhesives. If voids are created during the bonding cycle due to the release of volatiles, the adhesive strength of the bond may be decreased.

The development of thermoplastic polyimides has increased the processibility of polyimides in void free applications. St. Clair[22] reported on the development of a linear thermoplastic polyimide derived from 3,3'4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 3,3'-diaminobenzophenone (m,m'-DABP). This polyimide can be imidized and freed of volatiles at a relatively low temperature of 230°C compared with 300°C for conventional polyimides. Because of its meta-oriented backbone structure the polyimide can be processed as a thermoplastic after imidization and solvent removal. When bonding titanium adherends the above thermoplastic polyimide increases in strength after aging at elevated temperatures. Results indicate that the lap shear strength at 232°C increased 50% after aging 3000 hours at 232°C.

Shah[23] describes various properties, processing modes and applications for thermoplastic polyimides in general. Thermoplastic polyimides are resistant to high temperatures indicated by a glass transition temperature of 310°C for unfilled resins. Their elongation (10%) is indicative of good toughness. They are also resistant to most organic solvents and dilute acids. Various processing modes include:

compression molding, laminates, fibers and films. Major applications include use in the aerospace and electronic industries.

St. Clair[24] developed a solvent resistant, thermoplastic poly(imide sulfone). By incorporating the thermoplastic properties of a polysulfone with the solvent resistant properties of the polyimides, a polymer with good adhesive, molding and composite properties can be achieved. The poly(imide sulfone) has a meta-oriented backbone structure and can be processed in the 250° to 350°C range. By introducing various meta-oriented flexible units, the processibility of polyimides in void-free application is enhanced.

Another means to increase the processing involves synthesizing low molecular weight polyimides containing latent crosslinking groups such as acetylene. Polyimides containing latent crosslinking groups are classified as addition polyimides in the literature and shall be discussed in more detail below.

B. Addition Polyimides

As implied above, processing is an important criterion when choosing a polymer for a particular application. One method to improve processibility is to make the second step in the cure of polyimides an addition reaction. The maleimide, nadimide and acetylene functions are examples of latent crosslinking groups that have been incorporated into low molecular weight polyimides to improve processibility. Each of these crosslinking functionalities will be addressed separately, below. The synthesis and proposed mechanism by which the terminal functional groups crosslink will be reviewed. A brief discussion of the adhesive

and thermal properties of these polyimides will also be included.

The maleimide-capped prepolymer is synthesized by incorporating maleimide functions onto the end of short chained polyimides or by reacting a diamine with maleic anhydride to essentially form a new monomer (Figure 4). Two basic preparations for maleimides are cited in the literature. Several cited preparations[25-27] are based on the method of Searle[28] from a diamine and maleic anhydride. This patented process involves heating to 80°C while stirring N-arylmaleic acids with an excess of acetic anhydride and about 5-10% by weight of sodium acetate. The heating is then discontinued, but the heat of reaction increases the temperature of the solution to approximately 90°C in 5-15 minutes. After one hour the solution is poured over ice to precipitate the n-arylmaleimides. The other preparation involves dehydration of the amic acid prepolymer by using acetic anhydride and a basic catalyst such as sodium acetate[29] or triethylamine[30] at 0°C.

Chemical imidization is necessary when synthesizing maleimides because maleic acid is converted in part to fumaric acid when heated to temperatures slightly above its melting point, 130°C. Thermal conversion to fumaric acid prevents cyclization to the imide thus reducing the thermal stability of the final product.[29]

The maleimide-capped compounds can further react with diamines by a hydrogen addition reaction or can react by a heat induced self-addition which leads to crosslinking (Figure 5).[31] The reaction mechanism of only the heat induced self-addition reaction will be addressed below.

Kwiatkowski[30] hypothesizes that the mechanism of the thermally

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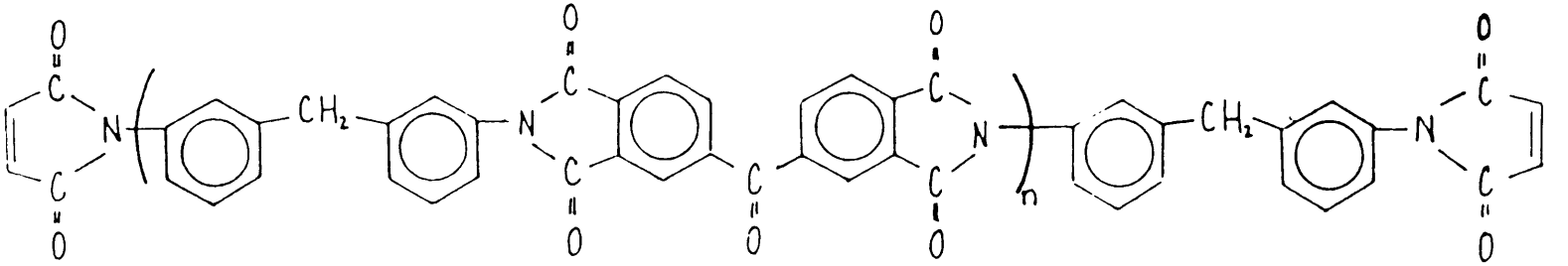

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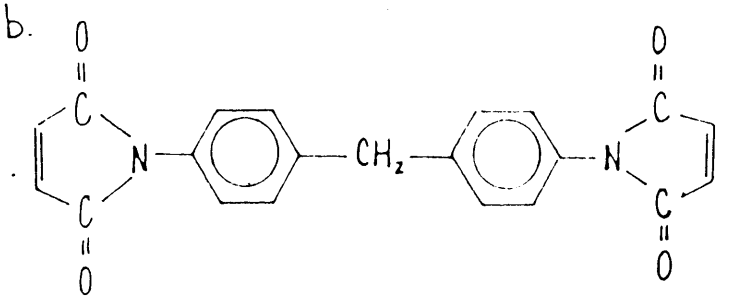


Figure 4. Examples of Maleimide End-Capped Prepolymers; a) Maleimide Functions on the End of an Oligomer, b) Maleimide Functions on the End of a Diamine

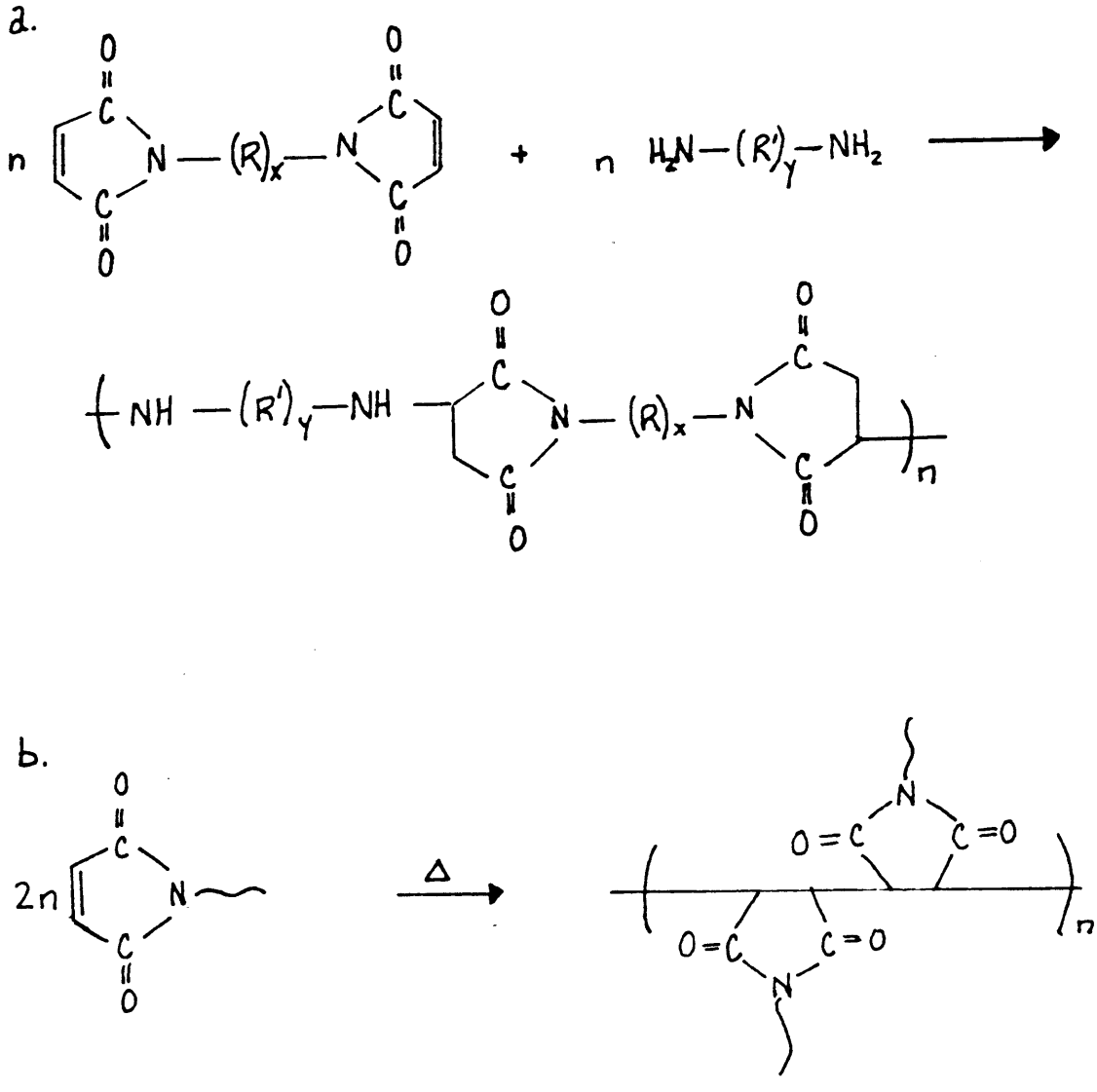


Figure 5. Polymerization Reactions of Maleimide-Terminated Oligomers: a) Via an Hydrogen Addition Reaction, b) Via a Heat-Induced Self-Addition Reaction

induced self-addition reaction of the maleimides involves a free-radical polymerization. Evidence cited for the above hypothesis is the marked increase in the cure rate with the addition of a free radical initiator. The cure rate of a diphenyl sulfone-based maleimide was increased from 80 minutes at 200°C without a peroxide additive to under five minutes at 200°C with 1.5% dicumyl peroxide as an initiator. There is a modest rate increase in the cure with the addition of amines or phenols, which may be a competing anionic Michael-type addition reaction. A Michael addition is the nucleophilic addition of a carbanion to an α,β unsaturated carbonyl compound.[32] Since maleimide-capped compounds are α,β unsaturated carbonyl compounds when they undergo anionic polymerization it can be considered a Michael-type addition.

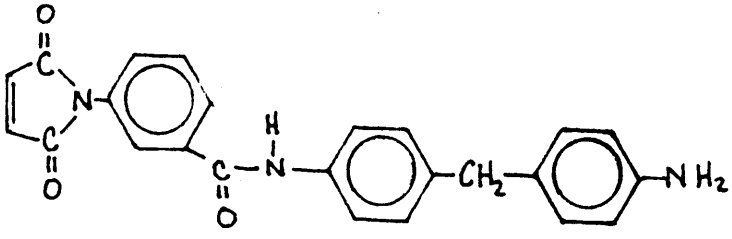
The resulting crosslinked polyimide contains aliphatic groups which may reduce the thermal stability of the final product. Kwiatkowski[30] was able to obtain lap-shear strength data at elevated temperatures with aluminum panels and a diphenyl sulfone-based maleimide. His results indicated that the tensile strength data at approximately 200°C were equivalent to room temperature data within experimental error. St. Clair[29] reports that at elevated temperatures the maleic-capped 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 3,3'-methylene dianiline (m,m'-MDA) polyimide oligomer resulted in failed lap shear specimens of titanium.

The major disadvantage of most bismaleimides is their brittleness due to their high crosslink density and the aromaticity of the materials employed for their synthesis. Stenzenberger[33] believed that the way to

overcome this problem was to increase the prepolymer molecular weight. This increase needed to occur in such a way that there was an increased elongation at break without losing a low temperature melt transition for easy processibility. These goals were achieved by reacting a monoimide with a bismaleimide (Figure 6) to achieve a high molecular weight linear prepolymer. The polymerization was controlled so that the free amino groups of the monoimide (I) react via a Micheal-addition with the bismaleimide (II) and then the resulting prepolymer crosslinked via a free radical addition reaction. In this way a lower crosslink density was achieved, thereby improving the strength and elongation properties of the bismaleimide.

The norborene function is another example of latent crosslinking groups that have been incorporated into low molecular weight polyimides to improve processibility via an addition reaction. 5-norborene-2,3-dicarboxylic anhydride is commonly referred to as nadic anhydride and is the end-capping agent that will be discussed below.

The nadic-capped imide prepolymers can be prepared from the diamine, nadic anhydride and a dianhydride in a 4:3:2.5 mole ratio under an nitrogen atmosphere. The diamine is dissolved in a solvent such as N,N-dimethylformamide (DMF) or N-methylpyrollidone (NMP). The nadic anhydride and dianhydride are then added as solids. By varying the order that incremental amounts of the above compounds are added to the dissolved diamine, different molecular weight distributions can be obtained.[29,34] The amic acid thus obtained is precipitated in water, dried and then thermally imidized. Imidization can also be achieved <u>in situ</u> chemically, followed by precipitation.



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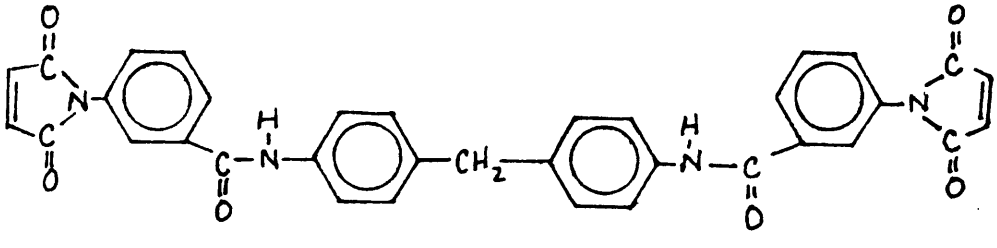

II

Figure 6. Reactants in Bismaleimide Resin Concept to Increase Prepolymer Molecular Weight (Ref. 33).

Gaylord[35] reported on a model study to determine the mechanism for addition-curing norborene end-capped polyimides. The experimental data support the hypothesis that radical polymerization occurs via a simple double bond self-addition.

Stenzenberger[33] reports that the cure of a nadimide is generally accepted to occur via a retrograde Diels-Alder reaction of the nadimide endgroup to generate maleimide endgroups and cyclopentadiene at high temperatures. The maleimide groups are believed to immediately proceed to copolymerize with cyclopentadiene and unreacted nadimide groups.

Several potential difficulties exist with the use of nadic-capped addition polyimides in void-free high temperature applications. The first problem is due to the presence of aliphatic groups present in the polyimide which may reduce the thermal stabiliity of the final product. The second difficulty arises from the possibility that the volatile by-product, cyclopentadiene, may escape before copolymerization (as described above) can occur. Curing nadic-capped imides under pressure tends to prevent the occurrence of the volatile by-product. St. Clair[29] reports that the nadic-capped polyimide derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and m,m'-methylene dianiline retains approximately 80% of its room temperature lap shear strength at 232°C (adhesive tests were performed on titanium). After aging the specimens for 1000 hours at 232°C the nadic-capped polyimide retained 75% of the original lap shear strength at 232°C, indicative of some polymer degradation.

The last functional group to be discussed in this review is the acetylene function. Acetylene terminated oligomers can be prepared by

either end-capping anhydride-terminated oligomers with ethynyl substituted aromatic amines[36,37] (Figure 7) or end-capping amine-terminated oligomers with an ethynl substituted aromatic anhydride[29] (Figure 8).

There is a commercially available acetylene terminated polyimide, Thermid® 600, sold by Gulf. Stenzenberger[33] reports that the molecular weight of the Thermid® 600 prepolymer can be adjusted so that the oligomer melts at around 200°C and polymerizes as soon as it becomes molten.

Bilow[36] reports that the crosslinking of acetylene-capped polyimides involves a trimerization to a benzenoid moiety. Hergenrother[38] measured the heats of reaction of several model compounds to verify if trimerization did occur. The experimental heats of reaction were found to be -38±0.7 kcal/mole, which is much lower than the estimated heat of reaction for the trimerization of acetylene to benzene which is -142 kcal/mole. If it is assumed that similar heats of reactions should be observed, the above results indicate that quantitative trimerization is not achieved in the model compounds studied.

Although some studies indicate that quantitative trimerization leading to aromatic moieties is not achieved, the acetylene-capped oligomers have shown good adhesive properties at high temperatures. St. Clair[29] reports that the adhesive properties of the acetylene-containing polymer (Figure 9a) with titanium adherends were excellent after aging at 232°C for 1000 hours. The lap shear strength was approximately 20% greater after aging than the initial high temperature measurement. In contrast, Bilow[39] reports that after aging for 1000 hours at 232°C, the commercially available acetylene end-capped polyimide, Thermid® 600

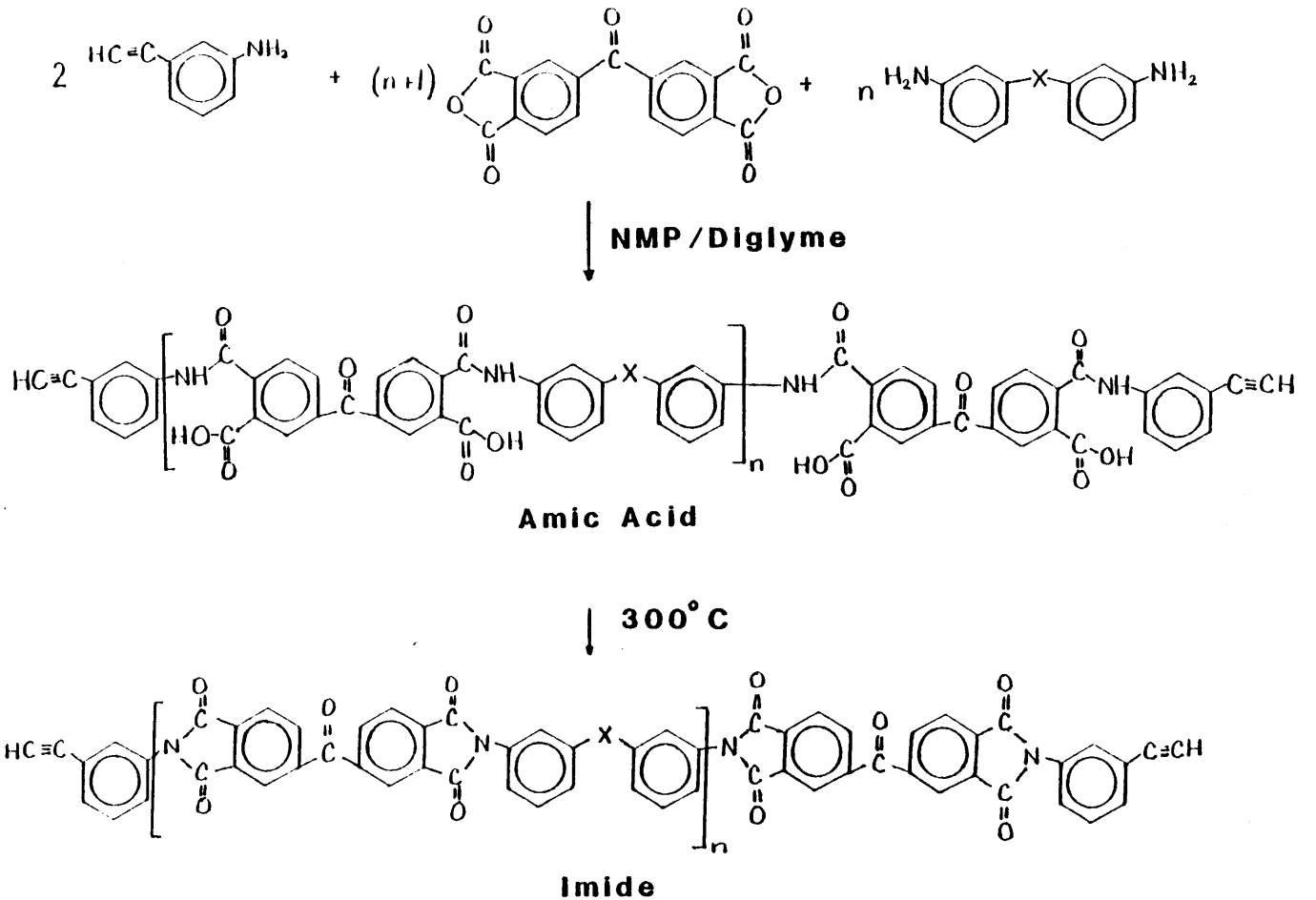

Figure 7. Reaction Pathway for Synthesis of Acetylene-Terminated Polyimide Systems-Ethynl Substituted Aromatic Amines (Ref. 37).

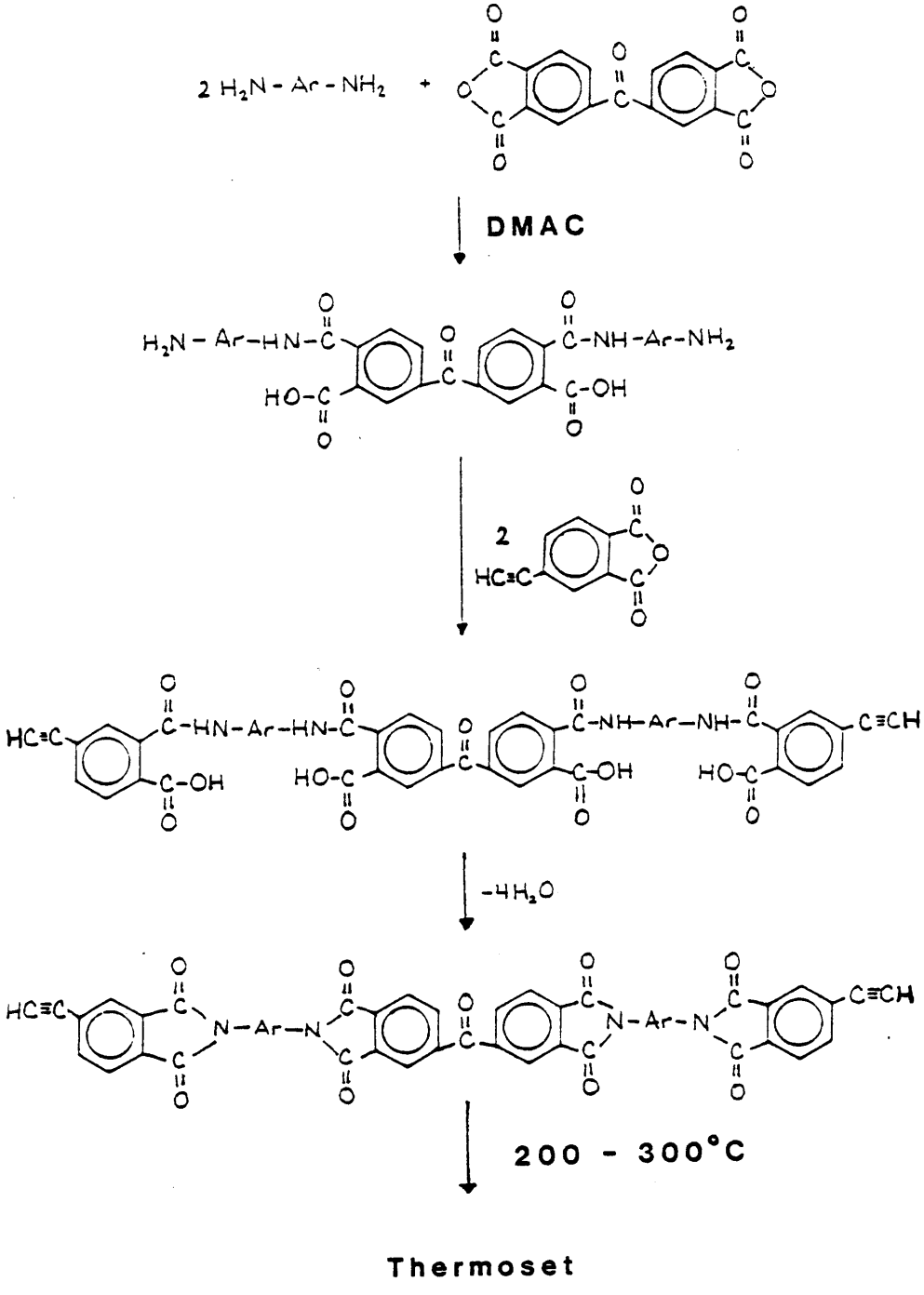

Figure 8. Reaction Pathway for Synthesis of Acetylene-Terminated Polyimides-Ethynl Substituted Aromatic Anhydrides (Ref. 29).

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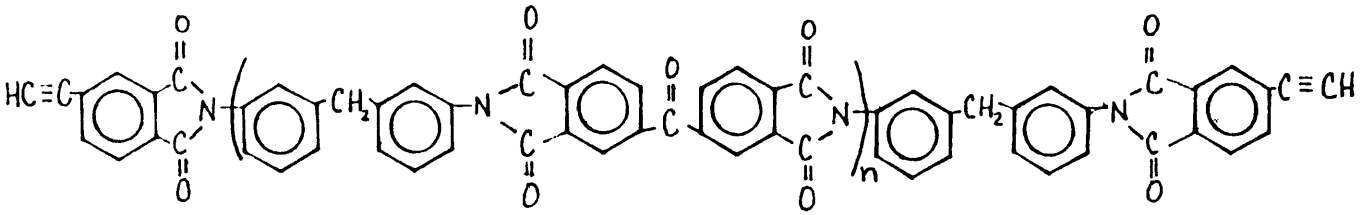

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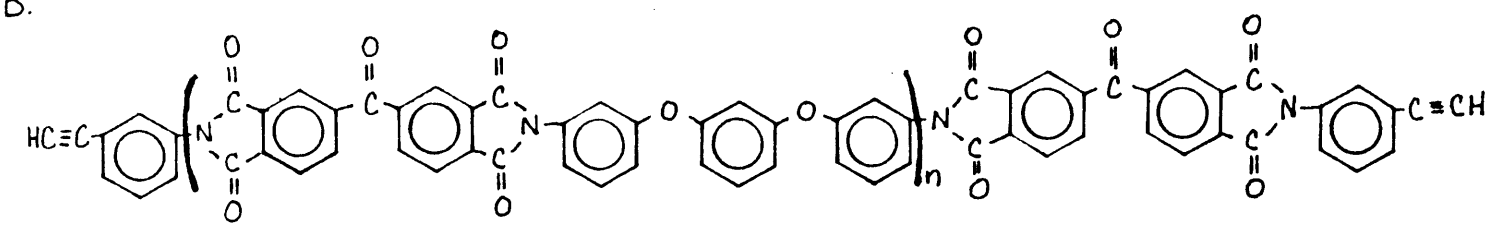


Figure 9. a) BTDA/m,m'-MDA Acetylene-Capped Polyimide, b) Thermid®600, the Commercially Available Acetylene-Capped Polyimide where n = 1.

(Figure 9b), with titanium adherends sustained a 45% loss in lap shear strength. By increasing the number of diamine and dianhydride units in the Thermid®600 polyimide, one each, the percent loss in lap shear strength after aging at 232°C is only 21%.

The above discussion has been a brief review of the literature addressing addition polyimides. The major mechanism for crosslinking appears to be a simple addition across the double bond by either radical or anionic polymerization. There appears to be some trimerization of the acetylene-capped polyimides due to the higher thermal stability of these compounds suggesting aromatic moieties. The adhesive properties of the addition polyimides have been shown to vary by changing the diamine, dianhydride and/or end-capping functionality. Lap shear strengths (Table I) at elevated temperatures ranged from failed specimens to slightly strengthened bonds. It also appears that improving the processibility by synthesizing low molecular weight polyimides containing latent crosslinking groups, such as acetylene, does not drastically reduce the thermal stabilities of polyimides at elevated temperatures of approximately 230°C.

C. Metal-Modification of Polyimides.

Polyimides have been modified via the incorporation of metal-ion complexes or metal particles into the polymer matrix. In this way adhesive, thermal and electrical properties have been affected. Thermal and electrical properties of metal-modified polyimides will be briefly reviewed below. The discussion relating to the effect of metal-fillers

TABLE I

Comparison of High Temperature Adhesive Properties of Various Polyimides

Polyimide	Lap Shear Strength (psi)	Lap Shear Strength After Aging 1000 Hrs @ 232°C	Test Temperature (°C)	Substrate	Ref.
BTDA[a]/m,m'-DABP[b]	1573	--[f]	250	titanium	14
BTDA/m,m'-MDA[c]/MA[d]	failed in heat-up	--[f]	232	titanium	29
diphenylsulfone-based maleimide	1330	--[f]	260	aluminum	30
BTDA/m,m'-MDA/NA[e]	2600	1960	232	titanium	29
Thermid® 600	2400	1200	232	titanium	39
BTDA/m,m'-MDA/acetylene	2500	2800	232	titanium	29

[a] 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride,
[b] m,m'-diaminobenzophenone
[c] m,m'-methylenedianiline
[d] maleic anhydride
[e] nadic anhydride
[f] aging test not performed

on adhesive properties will be included in the section on aluminum-polyimide adhesion.

Some of the thermal properties affected by metallic fillers are the glass transition temperature (T_g) and the polymer decomposition temperature (PDT). In general, fillers increase the T_g of the polymers, although, both lower and higher T_g's have been reported in the literature.[40] St. Clair[10] reports that the T_g of the polyimide derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and 4,4'-oxydianiline (ODA) increased approximately 30-40°C compared to the polymer alone with the addition of such metal-ion complexes as $AgNO_3$, Li_2PdCl_4, AuI_3 and $Al(acac)_3$. Ezzell[11] found that the amount of metal added affects the T_g's. Cu(I) dopants increased the T_g of the polyimide derived from BTDA and ODA when 2.6 or less wt.% was added. A greater percent copper caused a decrease in the T_g.

Not only does the amount of metal present affect the T_g's but the T_g's are also affected by the monomers used in the synthesis of the polyimide. The T_g of the polyimide derived from BTDA and ODA increased upon the addition of a Cu(II) complex. When the same dopant was added to the polyimide derived from pyromellitic dianhydride (PMDA) and ODA, a decrease in the T_g was observed. The curing atmosphere also appears to have an effect on the thermal mechanical data. Cu(II)-doped polyimides cured in air appear to contract prior to softening. When the Cu(II)-doped films are cured in N_2 no contraction is observed.

Polymer decomposition temperatures determined by thermal gravimetric analysis (TGA) can significantly change depending on the

dopant used. Bolger[16] reports that the PDT of a silver-filled polyimide resin is about 100°C less than the measured value for the polymer alone (550°C). The PDT of an aluminum-filled polyimide has been reported to be slightly greater than for the polymer alone. St. Clair[10] reports that $AgNO_3$ and Li_2PdCl_4 dopants reduce the PDT of the polymer along by greater than 100°C. Dopants such as AuI_3 and $SnCl_2$ have little effect on the PDT of the neat polymer resin. Cu(II) additives decrease the PDT of the polyimide (BDTA/ODA) from 540°C to approximately 440°C. Unlike the effect on thermal mechanical data, the curing atmosphere does not significantly change the PDT.

Metallic fillers not only affect the thermal properties of polymers, but may also enhance the conductive properties of a polymer from an electrical insulator to a good electrical conductor. In a theoretical discussion of the electron transport processes in conductive polymers, Sherman[4] described a loading curve of a typical conductor-filled polymer. There appears to be a critical point beyond which greater fraction of metal has little additional effect on the resistance. Aharoni[5] found the limiting value for iron powder in a polyimide-amide polymer matrix to be around 20 vol%. Aharoni also noted that the surface area of the filler played a role in the conduction. Equal volumes of carbon black with different surface areas showed that the conductivity was proportional to the surface area.

Two Japanese patents[6,7] deal with loading polyimide or polyimide derivatives with silver, tin and nickel metal. With 65-90 wt% silver, resistivities (10^{-5} Ω-cm) in the metallic range were reported. With

65-90 wt% of tin or nickel added to the polyimide, resistances (10^{-3} Ω-cm) in the semi-conductor range were measured.

The doping of polymers with metal-ion complexes for improving conduction has received some attention in the open literature. Success in achieving significant enhancement of surface and volume conductivity by the doping of polyimides with palladium-ion complexes has been reported in the recent literature.[8,9]

St. Clair[10] reports about a variety of metal-ion complexes used in doping polyimide films. Films containing $Al(acac)_3$, Li_2PdCl_4, $AgNO_3$, AuI_3 and $SnCl_2 \cdot H_2O$ were evaluated. Only the palladium-ion complex decreased by an order of six the volume resistivity of the polymer alone. The palladium-ion complex and a tin complex enhanced the surface conduction of the polymer alone by an order of at least eight.

Other studies dealing with metal-ion incorporation into neutral polymers have been conducted. Khor[12] studied the properties of lithium-ion containing polyimides. The findings showed a significant enhancement in the surface conductivity of polyimides when doped with lithium chloride. The enhancement appears to be a function of moisture uptake due to the presence of lithium on the surface. Since other lithium-ion complexes also cause increase surface moisture but do not enhance conduction, the mechanism of conduction is still under study.

Ezzell incorporated various copper dopants[11] and tin complexes[13] into polyimide matrices in an effort to enhance conduction in polyimides. Experimental results show that copper (II)-doped films enhance surface conduction by three to five orders of magnitude relative

to the polymer alone. The surface resistivity decreased from the insulator range without tin dopants to the semi-conductive range with tin present. The enhanced conduction was hypothesized to be caused by the presence of SnO_2 on the surface.

Thus, the literaure shows that polymer properties, such as thermal stability and conduction, can be modified by incorporating high concentrations of metal particles or significantly lower concentrations of metal-ion complexes into polyimide resins.

D. Aluminum-Polyimide Adhesion

The literature related to polymer-metal adhesion is too vast to discuss completely in this manuscript. Therefore, the following discussion will only deal with aluminum-polyimide adhesion and associated surface preparations of aluminum.

The research relating to aluminum-polyimide adhesion can be broadly divided into three categories: adherends, fillers and coatings. A brief review of some of the cited literature will follow.

Success in using polyimides to bond Al panels together has been recorded in the literature. Kwiatkowski[30] reports adhesive data for Al lap joints prepared with an addition polyimide, a diphenyl sulfone-based maleimide. He measured a lap shear strength of 1330 psi at 260°C. Work done by Polish scientists relating to bonding Al using condensation polyimides is cited in Chem Abstracts.[41] The delaminating strength at 20°C was found to be 160-230 kg/cm^2 for the Al-polyimide bonds. Pike[42] reports on work with the FM-34 polyimide adhesive. This condensation polyimide produced acceptable bonded joints with Ti as well as Al

adherends. Only data on the Ti adherends were cited. A European patent[43] deals with aromatic polyimides containing flexible diamine moieties as useful adhesives in bonding chromated Al panels. A lap shear strength of 2640 psi was achieved. The test temperature was not reported.

Al, Al_2O_3 and Al-ion complexes have been added to polyimide matrices to enhance adhesion to various substrates. Bolger[16] has done work with Al_2O_3 and Al doped polyimides for use as adhesives in semiconductor chips. He experimentally found that Al-filled polyimides were more thermally stable than Ag-filled polyimides. He reported that Ag-filled polyimides degrade more rapidly in air at >250°C than unfilled or Al-filled polyimides. Bolger hypothesized that these findings resulted from the high reactivity of the oxide surface on the silver filler. Ag_2O is more able to initiate polymer degradation because of its stronger basic property (>pH 12) than aluminum or aluminum oxide which have relatively neutral surfaces. As a strong base, Ag_2O, can function as a dehydrogenation catalyst in the decomposition of a polymer. Bolger's study indicates that reactive metallic fillers degrade the adhesive properties of polyimides as opposed to enhancement of adhesion with neutral fillers such a aluminum.

Taylor[14] found that the high temperature adhesive properties of the BTDA-m,m'-DABP polyimide with titanium adherends were enhanced significantly by the addition of tris(acetylacetonato)aluminum(III), $Al(acac)_3$, in a 1:4 (metal-ion:monomer) mole ratio. The $Al(acac)_3$ doped polyimide exhibited four times the lap shear strength of the undoped polymers at

275°C. This increase was compared to results reported in the literature where the lap shear strength was doubled at 250°C with 79% aluminum-filled polyimide versus the unfilled polyimide. Bilow[39] found that 20 wt% Al filler in Thermid® 600 reduced the overall loss in lap shear strength after aging at 260°C for 1000 hours by 32%. Blatz[17] reports that a polyimide adhesive solution containing 65 weight percent aluminum powder produces lap shear bond strengths of titanium and composite adherends well above NASA goal levels. These changes in lap-shear strengths upon the addition of metallic fillers is explained by Burgman[15] as a reduction in residual thermal stress by matching the coefficients of thermal expansion of the adhesive and adherends.

The category of coatings can be divided into two areas: Al coating a polyimide surface or polyimide coating an Al surface. The Russian literature contains work that deals with the Al-polymer interface resulting from vapor deposition of Al metal onto polyimide films. The published work cited in Chem Abstracts relates to the enhancement of adhesion via thermal treatment[44,45] of the metallized film or chemical treatment[46] of the polyimide surface. Actual data were not abstracted.

The literature relating to coating Al panels with polyimide films deals mostly with the use of polyimides as insulating dielectrics in semi-conductor devices. Miller[47] reports that the reactivity of the substrate has an effect on the durability of the protective polyimide film. Rothman[48] studied the feasibility of using polyimide films as a substitute for SiO_2 in insulating semi-conductor devices. He concludes that polyimides seem to be very satisfactory for the desired application.

Saiki[49] reports about a coupling method that improves polyimide adhesion to large-scale-integration surfaces. A SiO_2 integration surface was treated with an Al chelate agent and then the surface was coated with the polyimide resin. It was found that the adhesive strength of the polyimide did not degrade after exposure to 120°C at 2 atm pressure of pure water vapor for 300 hours. The use of the chelating agent also protected the aluminum from corrosion under the same conditions.

Another use for coating Al surfaces with polyimides was patented by Hueck und Buren[50]. They coated Al foil with poly(amic acid) to improve the adherence of plastics, paints and varnishes to the Al.

An important aspect of any type of adhesive joint is the effect of surface preparations on the joint's ultimate strength and durability. Minford[51] conducted a study on the effect of surface preparation on adhesive bonding of aluminum. He studied several different surface treatments: vapor degreasing; mechanical abrasion and vapor degreasing; chromate conversion coating; anodization; chromic-sulfuric acid etch; phosphoric acid-alcohol etch; and acid paste. He concluded that anodization produced the best durable joints. Minford also indicated that the chromic-sulfuric acid etch gave the highest initial strengths and the longest service life of the three acid etches. If the surface were mechanically abraded before vapor degreasing stronger and more durable bonds were made than if the surface were only vapor degreased alone. Carre[52] studied the effect of surface preparation on the surface energy of a substrate using an Al surface as a model. He found that

phosphatization treatment led to the highest dispersive component of the surface energy and the lowest surface polarity. These two surface characteristics gave the highest adhesion strength and the greatest durability in a moist environment.

Alcoa's desire to maximize electrical joint stability at optimum conductance by using a polymer matrix can be divided into two areas: (1) achieve low volume resistivity between aluminum adherends and (2) adhesively bond an aluminum substrate. The above literature review briefly discussed subjects which strongly relate to these areas. The research presented here deals with the first area described above.

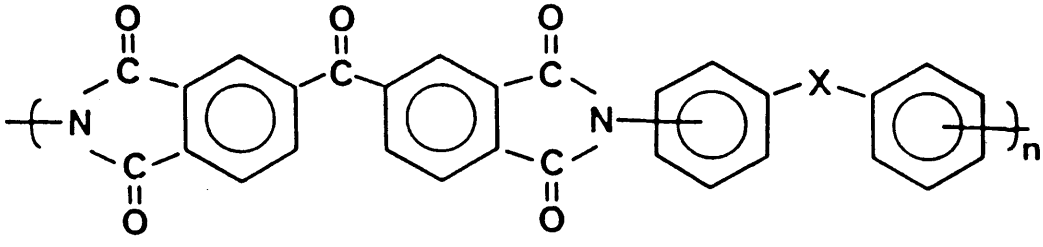
III. EXPERIMENTAL

A. Polyimide Systems

Two different types of polyimides, condensation and addition, were investigated as possible polymer matrices for application with electrical joints. The condensation polyimides were derived from 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride (BTDA) and one of the following diamines: 4,4'-oxydianaline (ODA), 3,3'-diaminobenzophenone (m,m'-DABP) and 2,2'-bis[4,(4-aminophenoxy)phenyl]-hexafluoropropane (4-BDAF). Figure 10 shows the structures of the above condensation polyimides. The addition polyimides which were synthesized, contained either maleimide or nadimide end groups. The bismaleimides were derived from maleic anhydride and one of the following diamines: 4,4'-methylene dianiline (MDA), m,m'-DABP and 4-BDAF (Figure 11). The nadimides were derived from nadic anhydride, BTDA, and either m,m'-DABP or 4-BDAF (Figure 12).

B. Metal-Ion Complexes and Metal Particles

The metal-ion complexes employed are tris(acetylacetonato)-aluminum(III), $[Al(acac)_3]$; dichloro-bis(dimethyl sulfide) palladium(II), $[Pd[S(CH_3)_2]_2Cl_2]$; bis(1,1,1-trifluoroacteylacetonato) copper(II), $[Cu(TFA)_2]$; and LiCl (Figure 13). An Al-Ni alloy (50/50 wt%) was employed for heterogeneous doping and shall be referred to as Alnox.



M,M'- DABP X= C=O

P,P'-ODA X= O

4-BDAF X= O

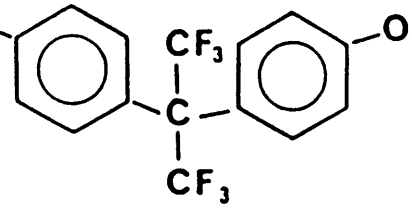
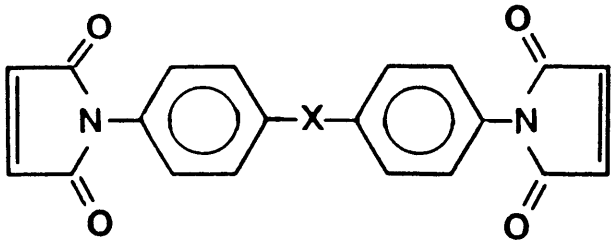


Figure 10. Condensation Repeat Unit.



P,P'-MDA X = $-CH_2-$

M,M'-DABP X = $>C=O$

4-BDAF X =

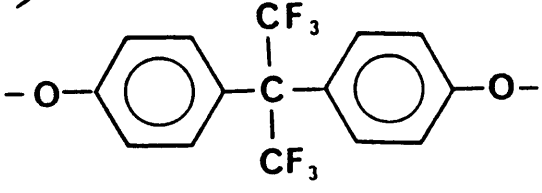
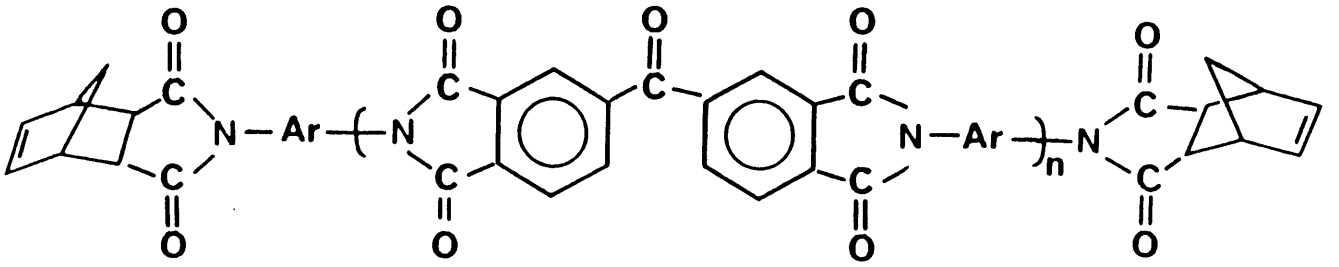
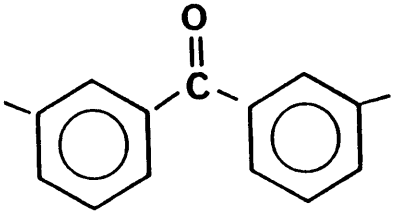


Figure 11. Bismaleimide Structures.



M,M'-DABP Ar =



4-BDAF Ar =

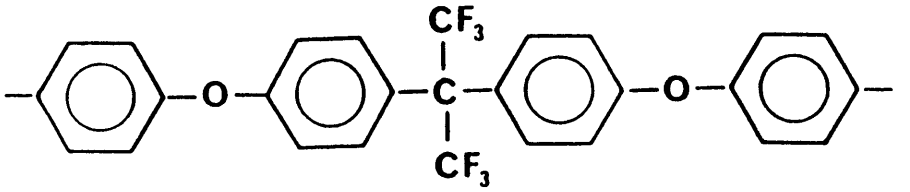
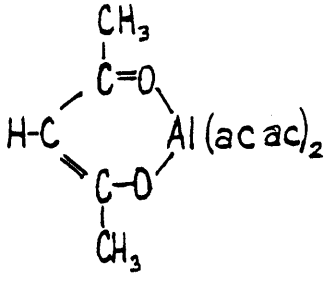


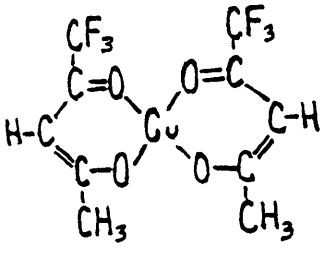
Figure 12. Nadic End-capped Oligomer Structures.



TRIS(ACETYLACETONATO)ALUMINUM(III)

$Pd(S(CH_3)_2)_2Cl_2$

DICHLORO BIS(DIMETHYL SULFIDE) PALLADIUM(II)



BIS(1,1,1-TRIFLUOROACETYLACETONATO) COPPER(II)

LiCl

LITHIUM CHLORIDE

Figure 13. Metal-ion Complexes Employed in Modification of Polyimides.

C. Materials Received

BTDA was received from commercial sources in a polymer pure grade and vacuum dried between 100-140°C for 2 hours before use (melting point, 558°K). ODA was obtained commercially and sublimed at 185°C at less than one torr pressure, melting point, 461-463°K (with decomposition). m,m'-DABP was obtained from commercial sources and vacuum dried at 100°C for 2 hours before use. 4-BDAF was obtained from Morton Chemical and used as received. 5-Norborene-2,3-dicarboxylic anhydride (nadic anhydride, NA) was received from commercial sources and used as received. Maleic anhydride (MA) was obtained commercially and used as received. The bismaleimide of p,p'-MDA was received already synthesized from T. St. Clair, NASA-Langley, and vacuum dried at 70-90°C for 2 hours before use. $Al(acac)_3$ was received from Aldrich Chemical Co. and LiCl was received from Baker Chemical Co. Alnox was obtained from Alcoa. $Pd[S(CH_3)_2]_2Cl_2$ and $Cu(TFA)_2$ were prepared according to literature references.[53,54] Reagent grade N,N-dimethylacetamide (DMAC), glass distilled and packed under nitrogen was obtained from Burdick and Jackson. N-methylpyrollidone (NMP) and bis(2-methoxyethyl)ether (diglyme) were obtained commercially and distilled over calcium hydride.

D. Polyimide Synthesis and Metal Modification

1. Condensation Polyimides.

The condensation polyimides were synthesized in the following manner. Four mmoles of the diamine were dissolved in DMAC. Upon dissolution,

four mmoles of the dianhydride were added with enough solvent, either diglyme or DMAC, to obtain between 18% and 27% solids. The metal ion dopant was added to the solution in a 1:4 (metal:monomer) mole ratio either before the diamine was dissolved or after the poly(amic acid) was synthesized. Metal particles were added in larger quantities and always after the poly(amic acid) was synthesized. The poly(amic acid) solution was stirred in each case under a N_2 atmosphere for at least six hours.

The poly(amic acid) thus obtained was either brush coated onto the Al bars or poured onto glass plates and spread with a doctor blade with a 16-20 mil blade gap to obtain a film which was subsequently used. The brush-coated specimens were heated at 60°C for approximately 40 minutes between each coat and 1.5 hours after the final coat to remove residual solvent. The films were initially dried at 60°C for approximately two hours in order to remove residual solvent. Thermal imidization was next accomplished by heating in a forced air oven at 100°C, 200°C and 300°C for one hour each. An additional curing cycle for the films was employed in an effort to perhaps increase the bonding capabilities of the polyimide. This cycle involved heating the cast film at 80°C for 20-30 minutes followed by thermal imidization at 100°C for one hour and approximately 225°C for two hours.

2. Bismaleimides.

The bismaleimides were prepared by using a modification of the method reported by G. Kwiatkowski[30] from the diamine and maleic anhydride in a 1:2 ratio as follows. To a 100 mL round bottom flask, equipped with a nitrogen inlet, was added 4 mmoles of the diamine and 10 ml of DMAC.

After dissolution of the diamine, the solution was cooled to 0°C. Eight mmoles of maleic anhydride were added as a solid in three equal portions. After one hour, excess acetic anhydride (6 mL) and fused sodium acetate (10 mmoles) were added. The flask was flushed with nitrogen and the solution was allowed to stir overnight at room temperature. The bismaleimide solution obtained was precipitated by addition to distilled water filtered and washed with a large quantity of water. The precipitate was vacuum-dried at 70°C - 90°C.

3. Nadic-capped Imide Prepolymers.

The nadic-capped imide prepolymers were prepared from the diamine, nadic anhydride, and BTDA in a 4:3:2.5 ratio as follows. To a round bottom flask, equipped with a nitrogen inlet, was added 8 mmoles of the diamine and 9-18 mL NMP. The diamine was allowed to dissolve. The 6 mmoles of nadic anhydride and 5 mmoles BTDA were then added as solids in three and five portions, respectively.[34] The final percent solids was between 15 and 20 percent. The flask was flushed with nitrogen and the resulting solution was stirred for approximately three hours.

The poly(amic acid) thus obtained was chemically imidized <u>in situ</u> using an acetic anhydride/pyridine mixture. One mL of acetic anhydride, 0.4 mL of pyridine, and 2 mL of solvent per four mmoles of diamine were added to the poly(amic acid) solution. The flask was flushed with nitrogen and the solution allowed to stir overnight. The imide prepolymer was precipitated with distilled water, ground in a Waring blender, filtered and washed with a large quantity of water. The precipitate was vacuum-dried at 70°C - 90°C for two hours.

E. Metal-Modification of Polyimides

The modification of the polyimides occurred in two ways. The first method involved doping with metal-ion complexes which shall be referred to as homogeneous doping. The second modificaton method involved doping with metal particles and shall be referred to as heterogeneous doping.

Condensation polyimides were doped homogeneously or heterogeneously at the poly(amic acid) state as described previously in section D. The polyimide powders, whether addition or condensation, were doped heterogeneously as described in section H.

F. Polymer Characterization

1. Visual Melt-Flow Properties.

Visual melt-flow properties of the addition polyimides were determined using a Fisher-Digital Melting Point Analyzer Model 355. Heating rate was 25°C/min. and/or 2°C/min.

2. Infrared.

Infrared spectra of the imide oligomers were obtained using a Perkin-Elmer Infrared Spectrophotometer Model 283B.

3. Preliminary Environmental Testing.

Isothermal stabilities of cured addition polyimides were determined by measuring the % weight loss after 100 hours at 200°C in a forced air oven.

Corrosive/Humidity stabilities of the cured polymers were determined by measuring the % weight loss after 100 hours in a 2% HF solution (v/v) at room temperature.

G. Electrical Joint Designs

The electrical joints used in this study were made from 2" wide, 1/4" thick aluminum bars (purity >99.6%) whose lengths were either 6" or 12". Between the Al bars were placed 2" square spacers made of Al. The joints were held together by an anodized Al bolt with washers and nuts (Figure 14).

H. Preparation of the Electrical Joint

1. Imidization Occurs in Bond.

The Al bus joint specimens employing this design were prepared as follows: (1) synthesis of the poly(amic acid) precursor as described previously, (2) fabrication of the Al bus joint, and, (3) thermal curing (300°C) to the polyimide. Fabrication of the actual joint involved: (1) cleaning the Al surface with acetone to remove gross contamination, (2) brush coating the poly(amic acid) solution onto the Al bars (usually three coats), (3) heating at 60°C for approximately 40 minutes between the first two coats and 1.5 hours after the final coat to remove residual solvent and (4) bolting the Al bars together (installing torque, 25 ft.-lb.). Thermal imidization was accomplished by step-curing at 100°C, 200°C, and 300°C for one hour each.

2. Bonding with Pre-formed Polyimide Films.

Two designs employed pre-formed films. The first design involved using a previously cured film doped with approximately 0.2 g of Alnox which had been cut to fit the two inch spacer. The second design involved cutting an undoped previously cured polyimide film into a gasket-like shape that fit the two inch spacer after which Alnox was

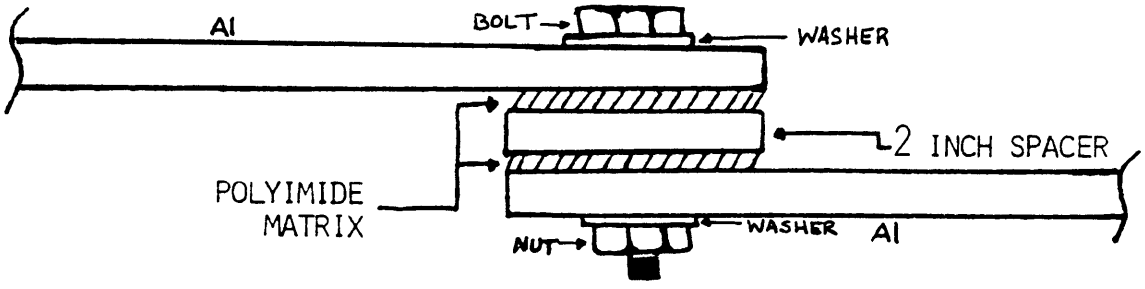


Figure 14. Schematic of Electrical Bus Joint.

spread on the exposed portion of the Al bar.

The Al bus joint specimens employing this general design were prepared as follows: (1) the film was cut into the desired shape, (2) placed between the Al bars (with about 0.1 -0.3 g Alnox for the gasket design), (3) bolted to approximately 30 ft.-lb. and (4) reheated to approximately 325°C for 0.25 - 4.0 hours.

3. Bonding with Pre-formed Polyimide Powders.

Two basic designs were also used with polyimide powders. The first design involved using the polyimide powders arranged in a gasket-like shape similar to that employed with the polyimide film. The second design used a uniform distribution of polyimide powder mixed with metal particles.

Two types of polyimide powders were used. The condensation polyimide powders were prepared as follows: (1) synthesis of the poly(amic acid) precursor as described previously, (2) precipitation of the precursor by the addition of distilled water, (3) grinding in a Waring blender, (4) vacuum filtration, (5) drying in a vacuum oven for approximately two hours at 90°C, (6) pulverization into a fine powder and (7) thermal imidization at approximately 225°C for two hours. The preparation of the addition polyimide powders was described earlier.

The electrical joints employing the gasket-like shape were prepared in a similar manner to the films described previously. The electrical joints employing the mixture of polymer powder and metal were prepared as follows: (1) homogeneous mixtures were made on a weight percent basis with a mortar and pestle, (2) the mixture was spread between Al

bars, (3) the bars were bolted to 30 ft.-lb. with C-clamps at the four corners and heated to either 200°C or 325°C depending on the polymer used.

I. Electrical Measurements

1. Room Temperature.

The resistance measurements were made using a Keithley 117 Digital Multimeter and a constant current source (Hewlett Packard 6200B). A constant current of 1 amp was passed through the Al bus joint specimens and the voltage drop across the interface was measured. This enabled us to achieve a lower limit of detection between 1 -10 μΩ. An average value of three resistance measurements was obtained for each joint prepared. The data tabulated here is an average value of the values obtained for two or more joints with the same matrix. If only one joint was prepared for a specific matrix no uncertainty was recorded.

2. High Current Cycling.

High current cycling was performed by T. Bond at Alcoa Laboratories, Electrical Products Division, Massena, New York. The high current cycling test involved passing current through an electrical joint test group (four joints per group) and then turning off the current. The current cycle is defined as passing current through the test group until the electrical joints reached an equilibrium temperature and then turning the current off until the joints cooled down to room temperature. The initial current load was 514 amps for 22 cycles. The current load was increased by steps until the final current load was approximately 1150 amps for 100 cycles.

IV. RESULTS AND DISCUSSION

Alcoa desires to maximize electrical joint stability at optimum conductance by using a conductive polymer matrix. The present industrial practice to obtain contact in the Aluminum electrical joints involves the use of a petrolatum based electrical joint compound.[55] It is the understanding of this author that the electrical joint compound contains a hydrogen fluoride precursor. Therefore, the chemistry which leads to good electrical contact may involve equations (1) and (2).

$$Al + O_2 \rightarrow Al_2O_3 \tag{1}$$

$$Al_2O_3 + 6HF \rightarrow 2\ AlF_3 + 3\ H_2O \tag{2}$$

The oxide layer reacts with HF to yield AlF_3. The AlF_3 produced may dissolve in the petrolatum matrix, thus exposing Al metal which subsequently reacts with more O_2 to produce Al_2O_3. The reaction, no doubt, can continue until the hydrocarbon matrix dries, thus preventing the AlF_3 from dissolving and the Al_2O_3 from reacting. Thus, the contact obtained via use of the electrical joint compound deteriorates over time, due to the petrolatum base evaporating and the subsequent build-up of the oxide layer. Electrical joint stability may be maximized by using a polymer matrix to achieve electrical contact. Since the temperature of the Al bus can reach 200°C in use, a polymer material which is thermally stable is needed.

Polymeric materials which have excellent thermal oxidative stability at temperatures greater than or equal to 200°C are polyimides

derived from an aromatic diamine and an aromatic tetracarboxylic acid dianhydride. Earlier research relating to the use of polyimides modified with metal-ion complexes or metal particles indicated that enhanced conductivity[6,8] and adhesive strength[14] can be achieved. The research being reported here evaluates the employment of metal-modified polyimides to achieve optimum conductance at an Al joint. Modification of the polyimides will be either by homogeneous or heterogeneous doping.

A. Polyimide Systems Employed

The condensation polyimide derived from ODA and BTDA doped with various metal-ion complexes previously used in our laboratories for other applications was initially employed. The second condensation polyimide system employed was derived from m,m'-DABP and BTDA which has been shown in the literature to be somewhat thermoplastic.[22] A third condensation polyimide system employed was derived from 4-BDAF and BTDA because of its reported thermal-oxidative stability.[56]

All of the above systems in fact exhibit good thermal-oxidative stability. These condensation polyimides are insoluble in conventional solvents, therefore, they are difficult to process. For this reason polyimides containing latent crosslinking functions, classified as addition polyimides, were also investigated for application with electrical joints.

The addition polyimide initially employed was derived from maleic anhydride and MDA. This polyimide was chosen because it thermally crosslinked around 200°C and should be crosslinkable in use. Its stability in the use environment of interest was unknown, therefore,

other maleic-capped polyimides derived from maleic anyhydride and either m,m'-DABP or 4-BDAF were also synthesized.

Nadic-capped polyimides have been reported to retain a good percentage of their original lap-shear strength after aging for 1000 hours at temperatures greater than 200°C.[29] For this reason, the nadic-capped addition polyimides derived from nadic anhydride, BTDA and either m,m'-DABP or 4-BDAF were also investigated.

B. Polymer Characterization

1. Visual Melt-Flow Properties

Visual melt-flow properties of the addition polyimides were determined using a Fisher-Digital Melting Point Analyzer, Model 355. Table II tabulates the data obtained. By varying the diamine used in the synthesis of the bismaleimides from m,m'-MDA to 4-BDAF or m,m'-DABP, a decrease in the melt range and an increase in the cure range were obtained. Whether this difference is due to the diamine or impurities present in the compounds is not known.

The nadimides which were synthesized, melted at temperatures around 200°C and their cure range was higher than the temperature limit of the melting point analyzer. Literature references report the cure of the nadimides to occur in the temperature range 270-310°C.[33]

2. Infrared

Infrared spectra of the imide oligomers were obtained using a Perkin-Elmer Infrared Spectrophotometer, Model 283B. Two spectra obtained from KBr pellets of the oligomers are included here for ease of reference. The other spectra of the oligomers, as well as, two spectra

TABLE II

Visual Melt and Cure Temperatures of Addition Polyimides Synthesized

Polyimide	Melt Range (°C)	Cure Range (°C)
Bismaleimide of p,p'-MDA	152 - 156	212 - 216
Bismaleimide of 4-BDAF	95 - 100	250 - 275
Bismaleimide of m,m'-DABP	85 - 105	200 - 260
m,m'-DABP/BTDA/nadic anhydride	210 - 215	>280
4-BDAF/BTDA/nadic anhydride	185 - 190	>250

of unimidized oligomers and a spectrum of the KBr used are included in the Appendix.

Most IR spectra of polyimides have a double band occurring around 1780 cm^{-1} and 1724 cm^{-1} due to the weak coupling of the carbonyl groups in the imide moiety.[57] This double band is very noticable in the spectra of the nadic-capped oligomers (Figure 15) and absent in the unimidized oligomer. Infrared spectra of an unimidized and imide version of the nadic-capped prepolymer can also be found in the literature.[34]

The double band is not as noticable in the bismaleimides (Figure 16) perhaps due to the imide moiety being more planar in the bismaleimide. If the imide moiety is planar, the dipole moment of the carbonyl groups will not be significantly different. Thus, the double band associated with the coupling of the carbonyl groups will not be as prominent in the IR spectrum. J. Crivello[26] published a spectrum of the bismaleimide of p,p'MDA which compares favorably with an IR spectrum obtained in this study, from a less concentrated KBr pellet. Other bands which are probably caused by vibrational modes of the imide moiety can be found at 1370 cm^{-1} and 1111 cm^{-1}. The broad band around 3500 cm^{-1} in the imidized addition polyimide spectra is caused by H_2O contained in the KBr. The relatively sharp bands found in the bismaleimides (Figure 16) at approximately 3500 cm^{-1} may be caused by weak intramolecular hydrogen bonding from unimidized moieties. The band at 3100 cm^{-1} may be caused by aromatic C-H stretches in the diamine moiety. The broad absorption between 3500 - 2000 cm^{-1} in the unimidized

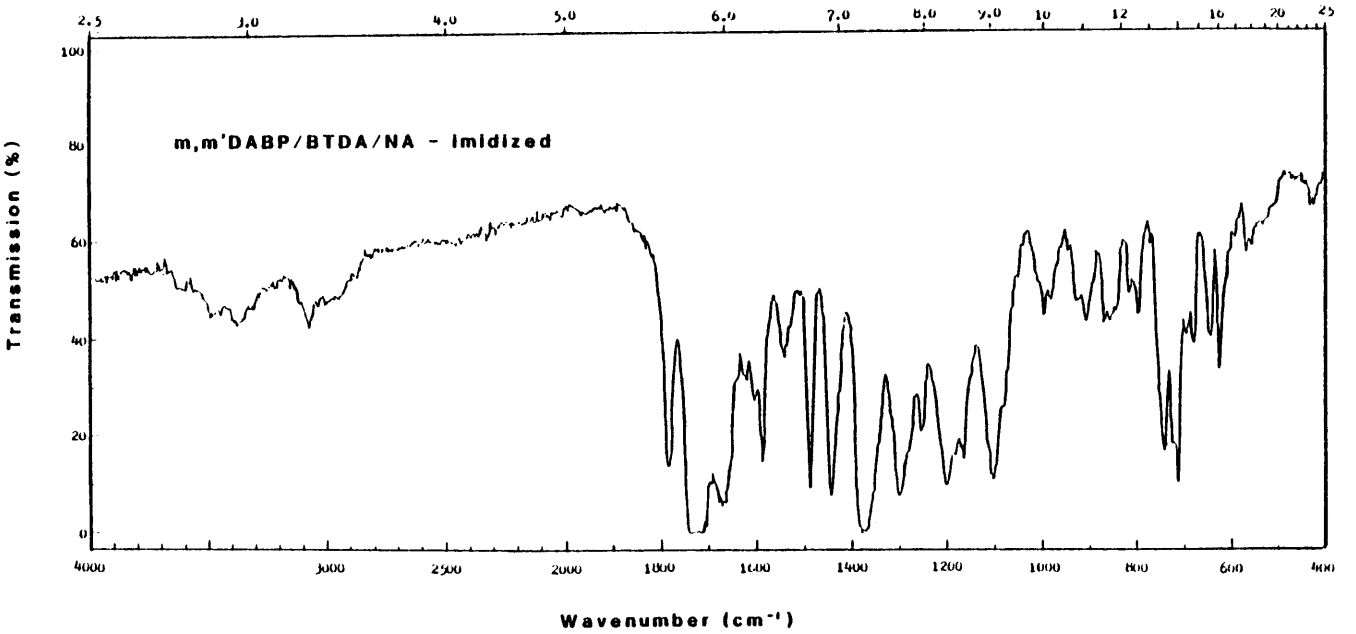


Figure 15. Infrared Spectrum of the Oligomer Derived from m,m'-DABP/BTDA/NA.

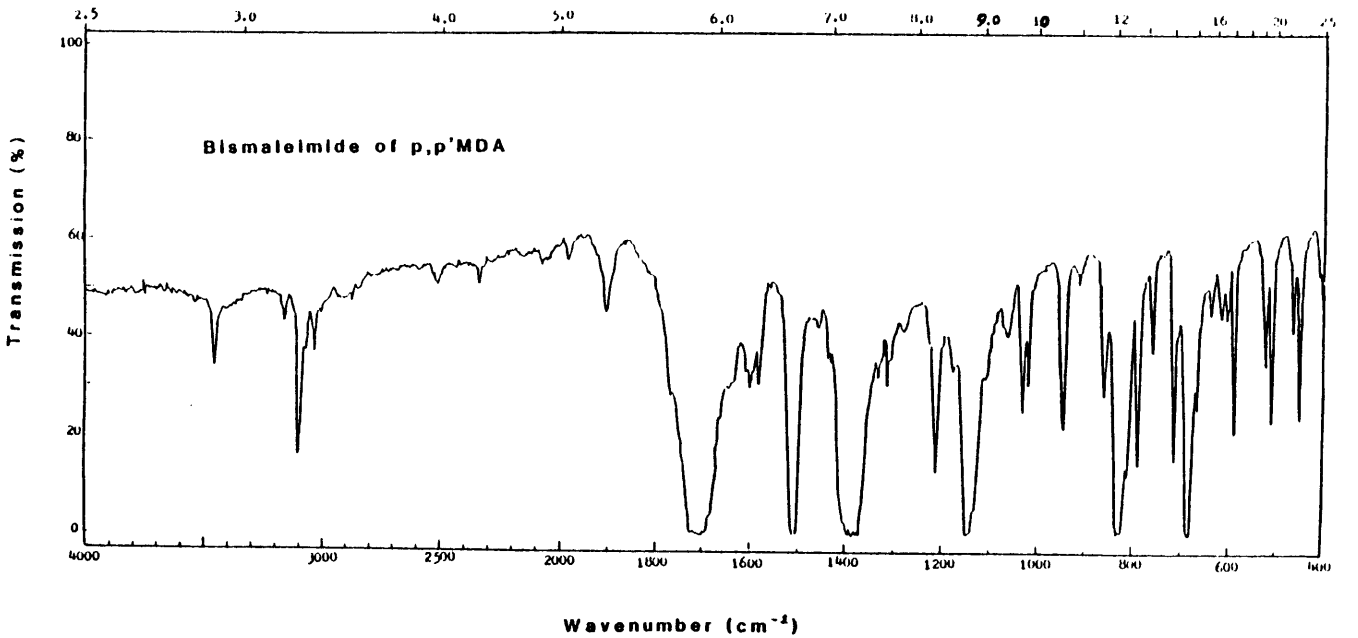


Figure 16. Infrared Spectrum of the Bismaleimide of p,p'-MDA.

addition polyimides is probably due to the intramolecularly hydrogen bonded carboxylic acid moiety in the poly(amic acid).

3. Preliminary Environmental Testing

Two preliminary environmental tests were done on the neat addition polyimide resin. Isothermal stabilities of cured addition polyimides were determined by measuring the % weight loss after 100 hours at 200°C in a forced air oven. The results are recorded in Table III. The differences in the % wt loss are not significant enough to ascertain if one oligomer is more thermally stable than another from this test.

Corrosive/humidity stabilities of the cured polymers were determined by measuring the % weight loss after 100 hours in a 2% HF solution (v/v) at room temperature. The results of this study are recorded in Table IV. The condensation polyimide derived from 4-BDAF-BTDA was also included in this test. Whether this test was valid is debatable since, some of the cured oligomers and the condensation polyimide film had densities lighter than the HF solution. What is interesting to note, is that, the average weight loss for the polyimides synthesized with the fluorinated monomer, 4-BDAF, was approximately 16% as opposed to 25% for the polyimides containing the monomer m,m'-DABP. The condensation polyimide or addition polyimides derived from 4-BDAF did not show significant differences in weight loss. This may indicate that the fluorinated polyimides are perhaps more stable in a fluorinated and/or a humid environment. The bismaleimide of p,p'-MDA was the most stable polyimide in the HF solution environment, perhaps due to higher purity resulting in a greater crosslink density thus, reducing the surface area in contact with the solution.

TABLE III

Preliminary Environmental Test - Isothermal Weight Loss Study[a]

Addition Polyimide	% Wt. Loss
Bismaleimide of p,p'-MDA	0.8
Bismaleimide of 4-BDAF	1.2
Bismaleimide of m,m'-DABP	3.4
m,m'-DABP/BTDA/nadic anhydride	0.5
4-BDAF/BTDA/nadic anhydride	1.9

[a]heated for 100 hours at 200°C

TABLE IV

Preliminary Environmental Test - Corrosive/Humidity Weight Loss Study[a]

Polyimide	% Wt. Loss
Bismaleimide of p,p'-MDA	6.9 ± 0.1
Bismaleimide of 4-BDAF	15 ± 3
Bismaleimide of m,m'-DABP	25 ± 5
m,m'-DABP/BTDA/nadic anhydride	26 ± 11
4-BDAF/BTDA/nadic anhydride	16 ± 10
4-BDAF/BTDA[b]	18 ± 1

[a]soaked for 100 hours in a 2% HF solution (v/v) at room temperature
[b]prepared as film

C. Electrical Measurements

The electrical joints used in this research effort were described previously (Figure 14). The present industrial practice to obtain good electrical contact involves the use of a petrolatum base electrical joint compound in the joint.[55] The bus joints are preliminarily prepared by (1) removing grease and dirt from the contact surfaces, (2) abrading the contact surfaces with a fine wire brush or abrasive cloth, (3) coating thoroughly with the electrical joint compound immediately after abrading, and (4) assembling the joint without removal of the compound. The contact pressure is between 750 and 800 psi. The temperature of the Al bus, in use, is approximately 200°C and the contact resistance is about 18 μΩ at 1 amp across the joint described earlier.[58]

The three basic electrical joint designs employing polyimide matrices are listed in Table V. The first design (I) employs homogeneous or heterogeneous doped condensation polyimides that were imidized within the assembled electrical bus joint. The second design (II) employs heterogeneously doped preformed condensation polyimide films that were placed between the Al bars before the electrical bus joint was assembled. The third design (III) used heterogeneously doped preformed condensation or addition polyimide powders. Undoped polyimide films and powders were also employed in modifications of the second and third designs. The initial designs are designated as II-A or III-A, while the modifications are designated as II-B or III-B. The modifications involved a gasket-like shape (Figure 17) permitting neat Alnox to be directly placed on the Al surface.

TABLE V

Electrical Joint Basic Designs
I. Bonding with imidization *in situ*
II. Bonding with pre-formed polyimide film
A. Cut to fit 2-inch spacer
B. Cut in gasket-like shape
III. Bonding with pre-formed polyimide powder
A. Mixed with metal particles
1. Condensation polyimides
2. Addition polyimides
B. Gasket-like shape surrounding metal particles

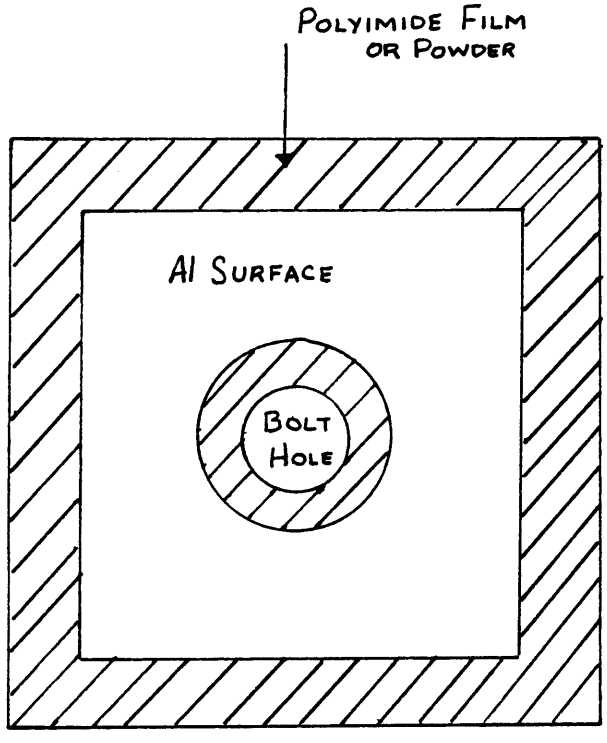


Figure 17. Schematic of a Two-inch Spacer with Gasket Design.

The resistance measurements for all designs were obtained by passing a constant current of 1 amp through the Al bus joint specimens and measuring the voltage drop across the interface. As shown in Figure 18, at each joint there was a jump in the voltage drop. This voltage difference is converted into the joint's resistance via the relationship described in Ohm's law. This method provided a lower limit of detection between 1-10 μΩ. Also, with a 4-point potentiometric method, the effect of contact resistance is avoided.[59]

Several reference specimens were initially assembled and their resistances are recorded in Table VI. For ease of discussion, the material placed between the aluminum bus bars will be referred to as the sample matrix. When no sample matrix was employed, a resistance of approximately 0.2 mΩ was measured. When undoped polyimides were used as the sample matrix, resistances between 0.2-3.0 mΩ were obtained. Due to the measurable resistance (2.3 mΩ) obtained when paper was used as the sample matrix, it appeared as if the bolt joining the two bars carried some of the current or that there is some residual surface conduction. When Alnox alone or the electrical joint compound was used as the sample matrix, resistances of 10 μΩ or less were initially achieved. Although this is the necessary contact resistance for the desired application, industrial use has shown that these two matrices are not conducive to long term use because the resistance increases over time. The resistances measured with the employment of Alnox alone or the electrical joint compound will be the point of reference in the employment of the polymeric matrices. Below follows a discussion

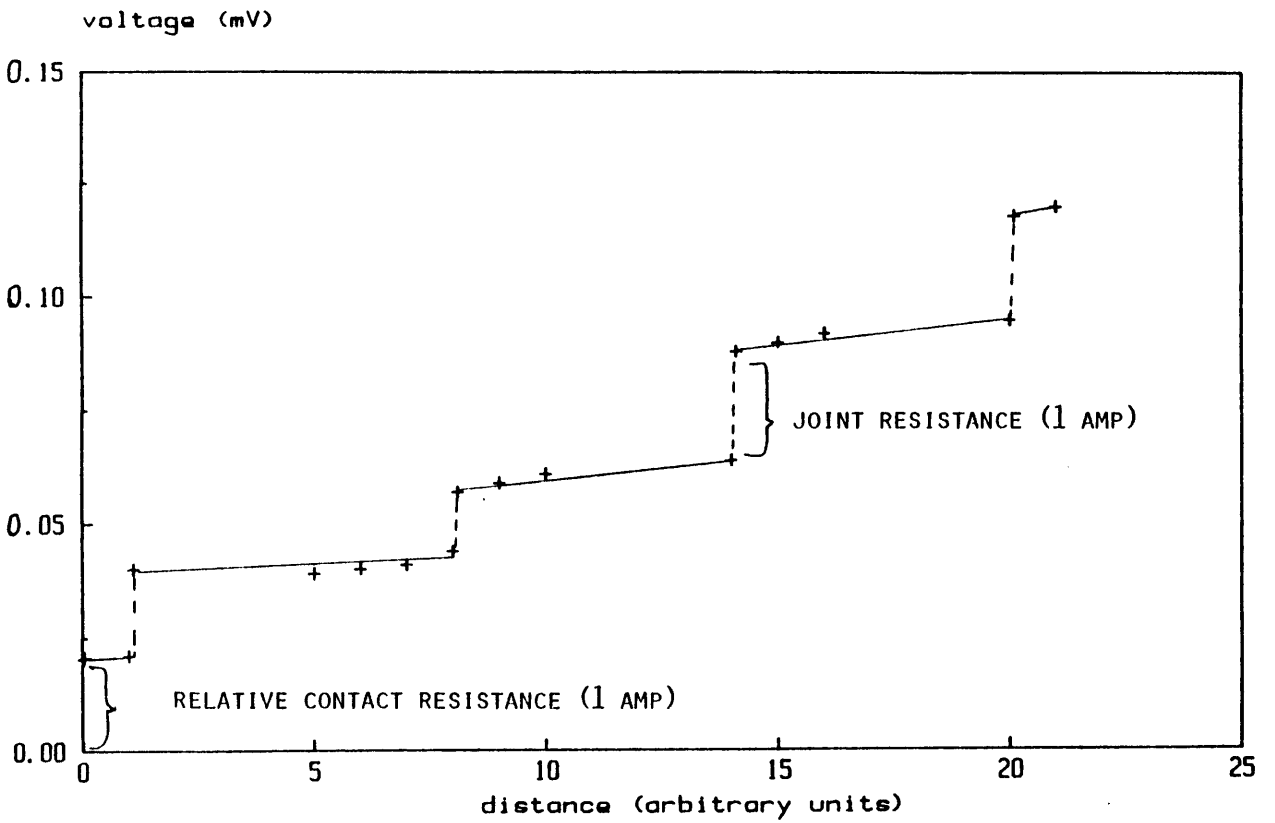


Figure 18. Voltage Difference Across an Aluminum Bus Test Group.

TABLE VI

Resistance Data of Reference Specimens

Sample Matrix[a]	Resistance
None	0.16 ± 0.11 mΩ
Polymer alone -	
Imidization in bond (Design I)	0.69 ± 0.11 mΩ
Pre-formed film (Design II-A)	1.6 ± 0.8 mΩ
Pre-formed powder (Design III-A)	0.70 ± 0.53 mΩ
Alnox	10 μΩ
Electrical joint compound (Alcoa No.2 EJC)	4 μΩ
Paper	2.3 mΩ

[a]sample matrix placed between Al bars in the electrical bus joint (refer to Figure 14)

related to our research effort of employing a polymer matrix to achieve conduction in an electrical bus joint.

1. Room Temperature Measurements

The ODA-BTDA polyimide doped with various metal ions was used in Electrical Joint Design I. The dopants, which were used, were $Al(acac)_3$, $Pd(S(CH_3)_2)_2Cl_2$, $Cu(TFA)_2$ AND LiCl. Duplicate Al joints were made for each dopant used. Resistances in the mΩ range were obtained (Table VII), with the bolt in place. The measured resistance (~1 mΩ) of the Al bus joint with the undoped polyimide sample matrix, was not reduced by the addition of the metal-ion complexes to the polyimide. Since no reduction was obtained, it was felt that the available metal ion complexes screened in our laboratory for other research projects, where surface conduction was achieved, were not applicable for the desired application. Therefore, the incorporation of Alnox into the polyimide system, used in Design I, was investigated. Although the weight percent metal loading was increased significantly, from 5% for the metal-ion complexes to 19% for the metal particles, the decrease in resistance, from 3mΩ to 0.3 mΩ, was not significant.

Many of the Design I specimens failed after several days in the laboratory environment after the bolt was removed. This seems to indicate that the curing cycle employed was not conducive to long term joint stability. The ineffective bonding of Design I was perhaps due to the evolution of water vapor in the bond line during the imidization step. If the poly(amic acid) was cured to the polyimide stage before the electrical joint was made, it was reasoned that we could circumvent

TABLE VII

Resistance Data of Aluminum Bus Joint Specimens Employing Design I - Imidization in Bond[a]

Dopant	Metal Loading (wt %)	Resistance (mΩ)
$Al(acac)_3$	1.3	5.0 ± 1
$Pd(S(CH_3)_2)_2Cl_2$	4.8	3.3 ± 2
$Cu(TFA)_2$	2.9	3.3 ± 2
LiCl	0.33	2.7 ± 2
Alnox	19	0.28 ± 0.04

[a] the polyimide employed was derived from ODA-BTDA

the problem associated with the bonding of materials together when using a polymer matrix in which volatiles are released upon curing. Two approaches were investigated. The first approach dealt with the use of a thermoplastic polyimide film doped with Alnox. The second method involved using an addition polyimide matrix. The discussion relating to the use of a thermoplastic polyimide is discussed below, while the use of addition polyimides is discussed later.

The m,m'-DABP polyimide system has been shown to exhibit better adhesive properties[22] than the p,p'-ODA-BTDA polyimide because of the increased flexibility provided by the meta linkage. Therefore, this was the polyimide chosen to use in Design II-A. Films with varying Alnox concentrations were made to find out how much Alnox could be added before the integrity of the polymer was lost. It was found that about 0.25 g Alnox per 4 mmole of monomer was the limit. Of the 0.25 g added to the poly(amic acid) solution, it was unknown as to how much Alnox was actually present in the cast film. The resistances measured for the Al bus joint employing heterogeneously doped polyimide films (0.4-8.0 mΩ) were similar to or greater than the values (0.8-2.2 mΩ) obtained with the undoped polyimide film (Table VIII).

Since Alnox alone (no polyimide) between the Al bars gives a resistance of 10 μΩ, the data for the polyimide doped Alnox may indicate several possible fates: (1) there is not enough Alnox in the film, or (2) the Alnox is not able to penetrate the film upon application of pressure, because the polymer film in which the Alnox is embedded is too thick. The above reasons led us to investigate a second design

TABLE VIII

Resistance Data of Aluminum Bus Joint Specimens Employing Design II-A - Pre-formed Films[a]

Weight of Alnox[b]	Resistance (mΩ)
0.00g	1.5 ± 0.7
0.20g	5.3 ± 2.8
0.25g[c]	0.38

[a] the polyimide employed was derived from m,m'-DABP-BTDA

[b] grams of alnox/10 ml 18.5% solids poly(amic acid) solution

[c] only one electrical bus joint was tested

involving polyimide films (Design II-B). By cutting an undoped polyimide film into a gasket-like shape that fits the two inch spacer, Alnox could be spread on the exposed portion of the Al bar (Figure 17). This should enable the achievement of resistances similar to the value obtained when Alnox was used without the polymeric matrix. When 0.1-0.3 g of Alnox was used with this design, resistances between 7-50 μΩ were obtained, comparing favorably with the 10 μΩ resistance obtained with Alnox alone.

Aluminum joints, employing Design II-A and II-B, were broken in an effort to elucidate the fate of the polyimide film during the bonding cycle. Visual inspection of the failed specimens indicated that the polymer adhered only in those areas under the washer (Figure 19). These observations led us to suspect that the washer, used when bolting together the Al bars, did not distribute enough pressure to ensure adhesion across the entire joint area. Therefore, a series of joints were made to determine if more pressure could be achieved at the edges of the joint. It was determined that C-clamps were needed at the corners of each joint in order to achieve the best bonding.

As a result of the above observations, it was felt that the relatively high resistances obtained using Design II-A were perhaps due to the fact that only a small area in the joint actually experienced metal-film contact. Thus, an Al joint employing Design II-A was made using C-clamps at the edges of the joint. A resistance of 4 mΩ was still obtained. Therefore, this design was no longer considered.

When Design II-B was prepared using C-clamps, bonding still did not occur around the edges. This observation appeared to indicate that the

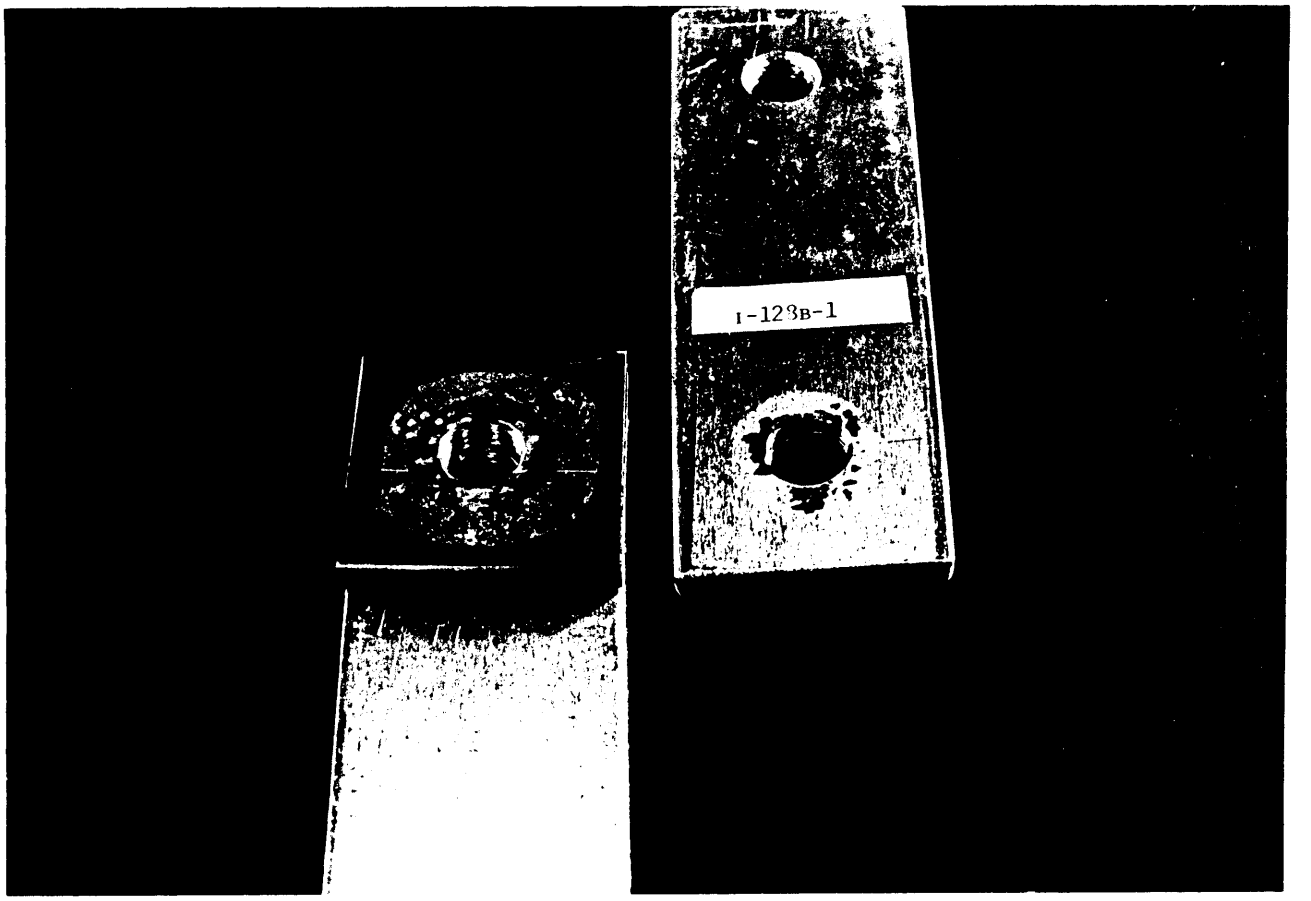


Figure 19. Photograph of Failed Al Bus Joint Specimen Employing Gasket Design.

Alnox layer was too thick to insure contact between the Al bars and the polymer film around the edges of the joint. Two approaches which provided lower resistances (7-50 μΩ) and the necessary bonding were found. The first approach used a thinner Alnox layer in Design II-B. The second approach was to make the polyimide in powder form and use the gasket design (Design III-B). With the second approach, the thickness of the Alnox layer would not be limited to the film thickness as is the case in Design II-B.

When using pre-formed condensation polyimide films and powders for bonding, the specimens needed to be maintained at temperatures greater than 300°C for excessively long times to achieve a bond. Therefore, addition polyimides were investigated as possible polymer matrices for application with electrical joints. Bilow[39] found that acetylene terminated addition polyimides have thermal stabilities at least equivalent to the condensation polyimides. St. Clair and St. Clair investigated nadimide end-capped addition polyimides,[29] as well as a variety of other latent crosslinking groups as end-caps[30]. Addition polyimides provide advantages over the condensation polyimides because the imide group is synthesized in a prepolymer form which is end-capped with terminal crosslinking groups. In this way, the weak bonding caused by the evolution of volatiles when employing condensation polyimides is avoided. The imide prepolymer undergoes thermal polymerization leading to crosslinking.

An Al joint specimen employing the gasket-like design with the addition polyimide 4-BDAF-BTDA-nadic anhydride was prepared (Design

III-B). A resistance of 17 μΩ was obtained. When the specimen was broken apart, failure appeared to have occurred in the polymer layer which is different than most of the other specimen's failure mode. Other Al joint specimens employing the gasket-like design with polyimide powders led to resistances between 7-50 μΩ.

Although the gasket design approached the microohm resistances required for the desired application, there was some concern that the polyimide "gasket" would experience excessive thermal stress due to the differences in the coefficients of thermal expansion of the polyimide and the Al metal. If this were the case, the thermal stress experienced could reduce the useful life of the seal formed by the polyimide "gaskets". Burgman[15] showed that the addition of metallic fillers to an adhesive reduces the residual thermal stress by matching the coefficients of thermal expansion of the adhesive and adherends. This reduction results in a stronger adhesive bond. Metallic fillers not only affect the adhesion but also affect the conduction of a polymer. Several patents[6,7] concerned with using Ag, Ni and Sn powders as additives in polyimide, poly(ester imide) and poly(amide imide) systems were granted. Heavy loadings (65-90 wt%) of the metal powders in the polymer system resulted in electrically conductive materials (10^{-3}-10^{-5} Ω-cm). These findings prompted the idea of mixing polyimide powders with metal particles (Design III-A).

Sherman[4] describes a loading curve of a typical conductor-filled polymer. There appears to be a critical point where a greater volume fraction of conductor has little effect on the resistance. This idea

led to an experiment where various amounts of Alnox were added to the polyimide matrix on a weight percent basis. In this manner one would be able to obtain the optimum conductance at maximum stability. For ease of understanding, maximum stability shall be defined as the point where additional Alnox has little effect on the measured resistance. Table IX shows the resistances obtained for a series of Al joints (without the spacer) prepared by varying the weight percent of Alnox and using the addition polyimide, bismaleimide of 4,4'-diaminophenyl methane. Figure 20 is the loading curve obtained by plotting the above data. It appears as if the point where additional Alnox has little effect on the resistances is between 60 and 80 weight percent.

To see if the polyimide had an effect on the resistances obtained, a series of electrical joints were prepared by varying the polyimide and keeping the weight percent of Alnox constant. Table X shows the resistances of specimens using both condensation and addition polyimide powders containing 80 weight percent Alnox. Duplicate joints were made for each polyimide employed. Resistances between 15 and 43 $\mu\Omega$ were measured. The results of the two tests, varying the wt% of Alnox and varying the polyimide matrix, seem to indicate that the resistance is more a function of the weight percent Alnox and not the polyimide.

A summary of the resistances obtained for the various designs is found in Table XI. It should be noted that the resistance between the Al bar and spacer is approximately one-half the value across the entire joint (refer to Figure 14) as reported here. The resistances are a function of these single-bolt double-lap joints in a two-inch Al bus and

TABLE IX

Resistances Obtained by Varying the Alnox on a Weight Percent Basis with the Bismaleimide of 4,4'-Diaminophenyl Methane (Design III-A)

Weight Percent Alnox	Resistance ($\mu\Omega$)
100	30
80	44, 10[a]
60	39
50	103, 244
40	503
20	823, 1615
10	906

[a] if two values recorded, two electrical bus joints were tested

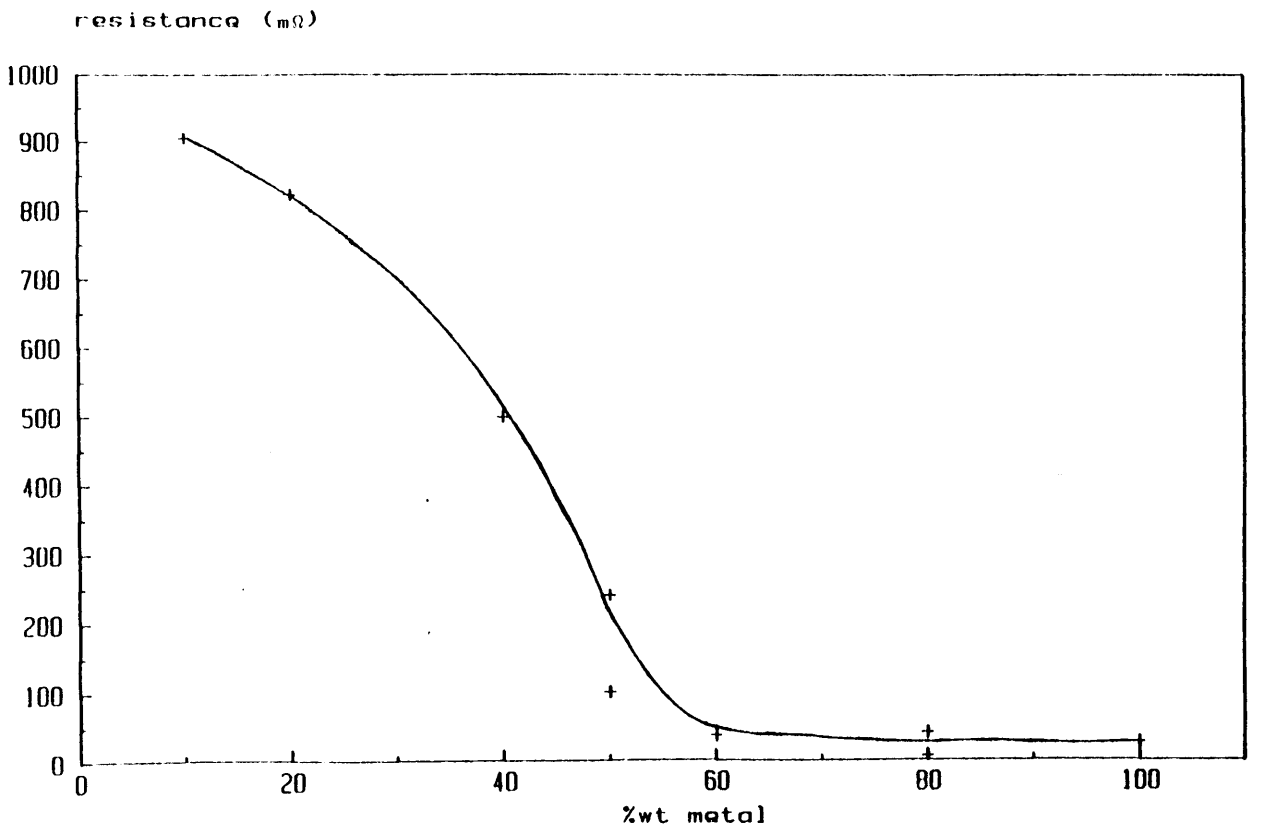


Figure 20. Resistance as a Function of Weight Percent Alnox in a Bismaleimide of p,p'-MDA Matrix.

TABLE X

Resistances of Specimens using Preformed Polyimide Powders Containing 80 wt% Alnox Powder (Design III-A)

Polyimide	Resistance (μΩ)
Bismaleimide of p,p'-MDA	17 ± 2
Bismaleimide of 4-BDAF	18 ± 2
Bismaleimide of m,m'-DABP	25 ± 2
m,m'-DABP/BTDA/nadic anhydride	38 ± 5
4-BDAF/BTDA/nadic anhydride	38 ± 5
4-BDAF/BTDA	30 ± 2
m,m'-DABP/BTDA	29 ± 3

TABLE XI

Comparison of Various Electrical Joint Designs

Design	Metal Loading	Resistances
Imidization in bond (I)	0.3 - 5 wt%	0.7 - 5 mΩ
Pre-formed films - spacer (II-A)	7 - 10 wt%	0.5 - 10 mΩ
Pre-formed films - gasket (II-B)	0.1 - 0.3 g/side	7 - 50 μΩ
Pre-formed powders - wt% (III-A)	80 wt%	17 - 38 μΩ
Pre-formed powders - gasket (III-B)	0.3 g/side	7 - 50 μΩ

should not be compared, as is, to other electrical joints. As can be seen, electrical joint Designs I and II-A have resistances similar to those obtained with undoped polyimides (~1mΩ). Designs II-B, III-A and III-B approach the resistances measured when using Alnox or the electrical joint compound without the polymer. Therefore, these designs (II-B, III-A, III-B) should be more thoroughly investigated.

The role of the bolt in the electrical joint was debated several times throughout this research effort. The bolts used in the electrical joints were anodized to prevent the major portion of the current from passing through the bolt. Examination of the bolt, before it was heated through the cure cycle and after, revealed that the greenish coating caused by anodization disappeared upon heating. The resistance of the bolt was measured using a Keithly 117 Digital Multimeter. The resistance, 0.11 Ω, decreased upon heating through the cure cycle to 0.019 Ω. Whether or not this indicates that the bolt plays a role in the current passage is not conclusive.

The resistances of specimens without the bolt were measured in an effort to elucidate more fully the role of the bolt in the electric joint. Table XII summarizes the resistances obtained. Design I (imidization in bond) and Design II-A (pre-formed films cut to fit spacer) had a large increase in the measured resistances, thus, indicating that the bolt played some role other than as a mechanical fastener in these designs. It appears as if the bolt is the path for current passage when the resistance across the face of the joint is too high. The measurable resistance obtained when paper was inserted between the Al bars also appears to support this reasoning. The fact

TABLE XII

Resistance Data of Aluminum Bus Joint Specimens Without Bolt

Design	Resistance
Imidization in Bond (Design I)	$> 0.3\ \Omega$
Pre-formed Films - condensation (Design II-A)	10^{-3} - $10^{0}\ \Omega$
Pre-formed Powders - addition (Design III-B)	32 - 34 $\mu\Omega$

that a measurable resistance is obtained without the bolt indicates that some contact is made across the face of the joint.

Design III-A (pre-formed powder, wt % basis) without the bolt has resistances similar to those obtained with the bolt. This seems to indicate that the current is passing through the face of the joint as opposed to the bolt. This result, also, seems to indicate that a good adhesive bond is achieved. Although no quantitiative adhesion data of the various designs were obtained, a qualitative assessment was made (Table XIII). Qualitatively, the addition polyimide gives the strongest bond. Future work relating to this research should deal with quantitative adhesion studies. The achievement of a stronger adhesive bond when using an addition polyimide is more than likely caused by the bonding method employed. In Design I, water vapor was released in the bond line causing voids which can result in a weak bond. Pre-formed condensation polyimides (Design II, III-A1) do not flow easily and therefore appear to bond via a sintering process instead of a wetting process. If there isn't enough applied pressure when using a condensation polyimide, a good bond is not made. The addition polyimides melt at relatively low temperatures (<220°C) and therefore appear to have the capability of wetting the substrate surface in the bonding process. If wetting does occur, a stronger bond can be achieved.

It would appear that addition polyimides are more processible for the desired application. Of the addition polyimides, the bismaleimides may be the ones of choice because the literature[33] has shown that these

TABLE XIII

Qualitative Assessment of Adhesion of Various Designs

Design	Ease of Breaking Bond
Imidization in Bond (I)	Easy
Preformed Films (II)	Fairly Difficult
Preformed Powders-condensation (III)	Easy
Preformed Powders-addition (III)	Difficult

compounds are soluble in lower boiling solvents than the nadimide or acetylene-capped oligomers.

Most of the addition polyimides thermally crosslink at temperatures between 200°C-300°C. Although the electrical joints can reach 200°C due to current passage, it may be several months before this temperature is achieved. Therefore, an outside heat source would be needed to initiate the cure. Studies cited in the literature indicate that a free radical mechanism is involved in the cure of bismaleimides.[30] Therefore, future studies should include work related to the cure of the addition polyimides, especially thermal cures with and without the presence of a free radical initiator.

2. High-Current Cycling.

Since the electrical joints are held together by using a bolt, we are not necessarily concerned with finding a structural adhesive, but rather a polymer matrix to protect the Al surface as well as to provide a path for the electrical current. Thus, a decrease in lap shear strength, although indicative of polymer degradation, may not be the ultimate measure of utility. A large decrease in lap shear strength may be acceptable as long as the resistance does not increase, over time, above an acceptabile limit. Therefore, the major measure of utility will be the monitoring of resistance change during the aging process.

Two electrical joint test groups, as shown in Figure 21, were sent to Alcoa Laobratories for high current cycling. Test group #218 employed electrical joint Design II-B using a 4-BDAF-BTDA film cut in a gasket shape and 0.1 g Alnox per side of spacer. Test group #229

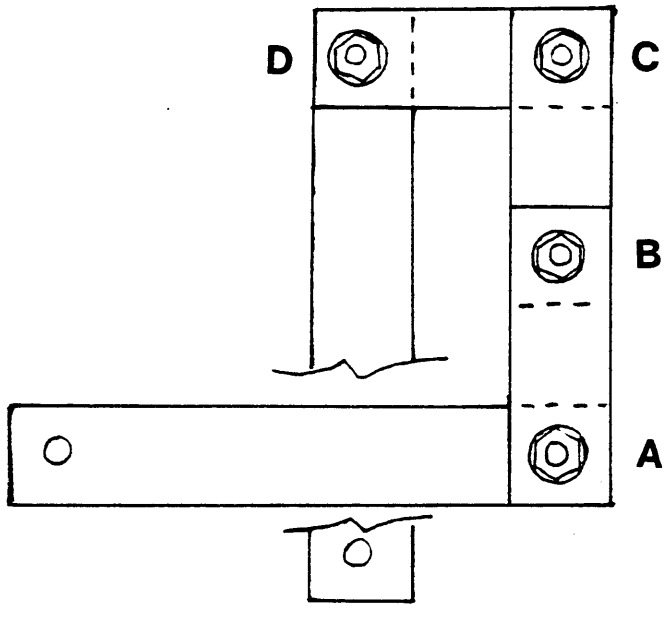


Figure 21. Schematic of Electrical Test Group.

employed gasket shape, Design III-A, using approximately 0.15 g 4-BDAF-BTDA-NA polyimide powder and 0.3 g Alnox per side of spacer. The average value of three room-temperature resistance measurements (our laboratory) obtained for each of the four joints in test group #218 was between 7-8 μΩ. The values obtained for test group #229 were between 5-9 μΩ.

Tables XIV and XV summarize results of resistance and temperature measurements in the high-current cycling test. A current cycle is defined as the current being on for one and one-half hours to two hours and one and one-half to two hours off. The current load ranged from 504-1176 amps (AC). The joints have been subjected to 444 current cycles, as of March 1984. The contact resistances in Table XIV are recorded in terms of Percent of the Acceptability Reference Level (PARL). The Acceptability Reference Level (ARL) is the contact resistance of a five diameter length of the conductor. A conductor with a value of 50 PARL for its contact resistance (Rc) has a resistance half that of the ARL. A conductor with such a Rc is suited for stringent applications, such as a simple bolted overlap connection in a bus conductor.[60] The value of ARL for the single-bolt double-lap joints in the 2-in Al bus used in this study is calculated to be 8.3 μΩ.[61] The average PARL value for the two test groups is approximately 60 PARL which is greater than the 50 PARL suited for stringent applications. The significantly higher contact resistance of joint B in both groups (~70 PARL) should be noted. This difference is attributed to the fact that these joints were "straight-through" rather than "right-angle"

TABLE XIV
Resistance Summary - High Current Cycling

Test Group[a]	Test Joint	Contact Resistance, Percent Acceptibility Reference Level (PARL) After Current Cycles Shown									
		0[b]	21	50	100	200	241	267	342	368	443
218	A	55	55	55	55	55	55	55	54	56	56
Design II-B/ 4BDAF-BTDA	B	69	68	69	69	69	69	70	70	70	70
	C	61	60	61	66	66	66	68	68	68	66
	D	52	52	54	52	53	52	52	52	51	48
	Avg	59	59	60	60	61	60	61	61	61	60
229	A	61	60	61	61	61	61	61	61	62	62
Design III-A/ 4-BDAF-BTDA-NA	B	68	67	68	67	67	68	68	70	70	70
	C	57	57	57	58	58	58	58	58	57	58
	D	56	56	56	56	56	55	56	57	57	57
	Avg	60	60	60	60	60	60	61	62	62	62

[a] both designs employed gasket-like shape
[b] number of cycles. One cycle is equal to high current on for two hours, high current off for two hours. Refer to Table XV for current loads.

TABLE XV

Temperature Summary: High Current Cycling

Test Group	Test Joint	Equilibrium Temperature Rise, °C, During Current Cycle Shown									
		1	22	51	101	201	241	268	342	369[b]	444
218	A	36	35	48	51	47	86	130	138	171	162
	B	37	36	48	52	48	90	136	145	190	170
	C	37	36	47	52	48	90	134	150	208	168
	D	38	37	49	50	47	89	132	152	236	175
	Avg	37	36	48	51	48	89	133	146	201	169
229	A	37	35	50	52	48	87	132	129	156	164
	B	38	37	51	54	49	90	135	134	158	167
	C	39	37	51	54	49	91	134	132	155	163
	D	39	37	51	54	49	92	132	126	149	159
	Av	38	36	51	54	49	90	133	130	154	163
Conductor Temperature:		30	29	40	41	38	68	104	109	124	131
Ambient, °C:		27	28	24	27	26	23	26	24	25	26
Circuit Current, amps:		504	504	612	612	612	900[a]	1080	1080	1152	1176

[a] only one cycle at 900 amps

[b] during 26th cycle of 101 cycles of 1152-1176 amps

joints as shown in Figure 21. The bulk metal resistance constant used in processing the data was not changed to reflect the difference between these two types. Since the original intention had been that all overlap joints be of the straight-through type, it appears that the data from joint B in both groups should be used to compare with future work.

Although the contact resistance of joint B in both groups was significantly higher, the equilibrium temperature (Table XV) was not significantly different from the temperatures of the other joints. The jump in the equilibrium temperature from the different groups of cycles is due to the change in the amount of current passed through the conductor. The higher temperatures of test group 218 compared with group 229 at 369 cycles was caused by a deteriorating current connection to the end of the group. The current connection was repaired before the final set of measurements.[61] The difference between the average temperature of the test joints and the temperature of the conductor increased from 10 to 40°C as the current load increased from 504 to 1176 amps.

Although the contact resistance is higher than would generally be accepted, the resistance stability is excellent. Therefore there is definite promise for using a polyimide matrix in this format for typical applications.

V. CONCLUSIONS

The results of this initial study seem to indicate that there is promise in the use of a polyimide matrix to maximize electrical joint stability at optimum conductance. The room temperature electrical measurements indicate that the lowest resistances are obtained using addition or condensation polyimides in the gasket design and polyimide/metal mixtures. These resistances, less than 50 μΩ, approach the resistances obtained with the electrical joint compound, which is less than 10 μΩ. High current cycling tests show that the gasket design appears to be stable. Although the resistances are not yet optimized, the stability of the joints indicate that the design shows promise. Qualitatively, addition polyimides appear to give the strongest adhesive bond for this particular application.

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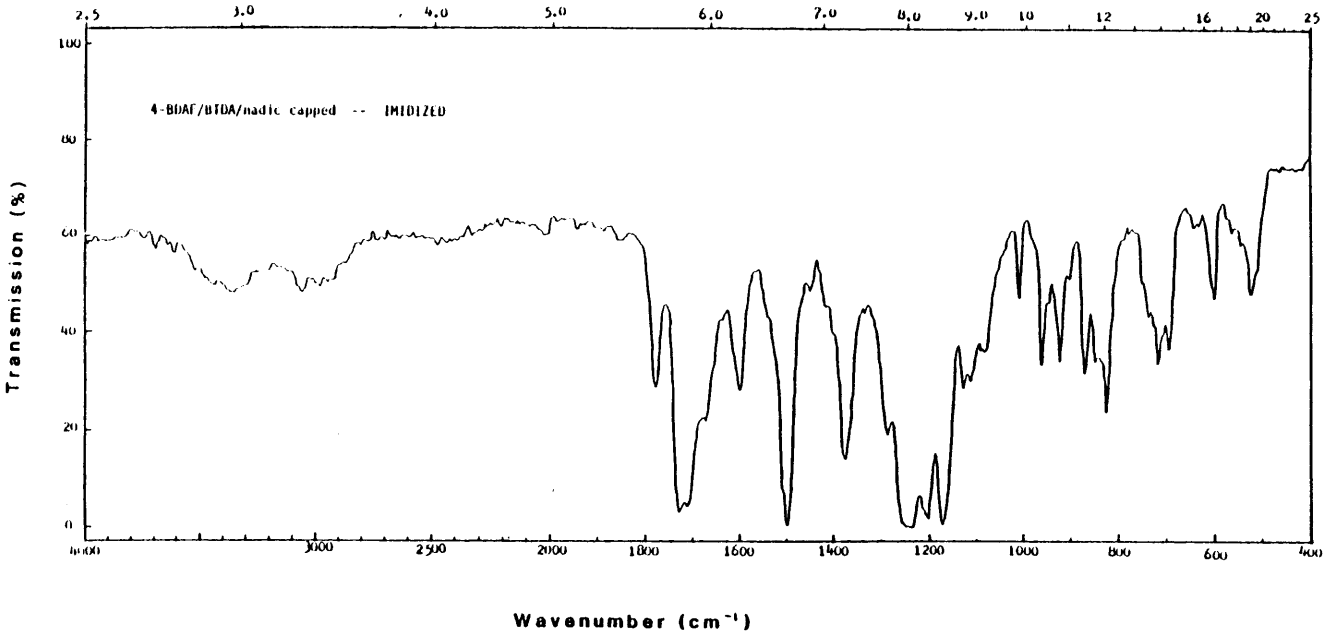
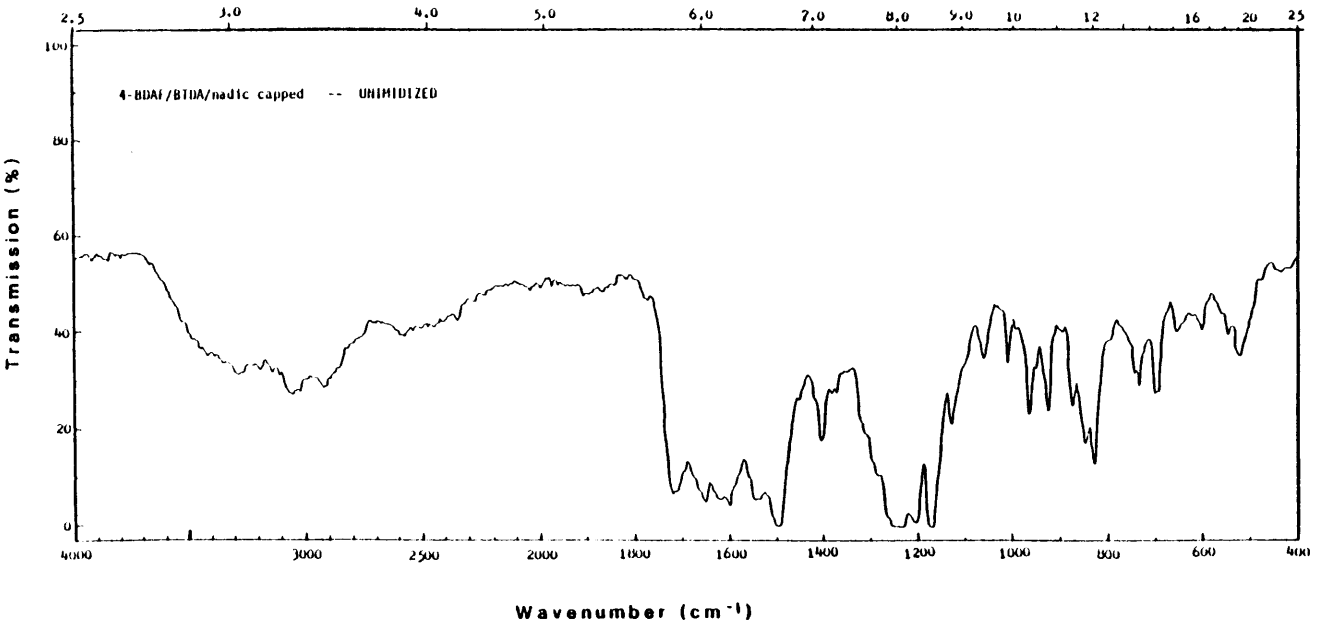
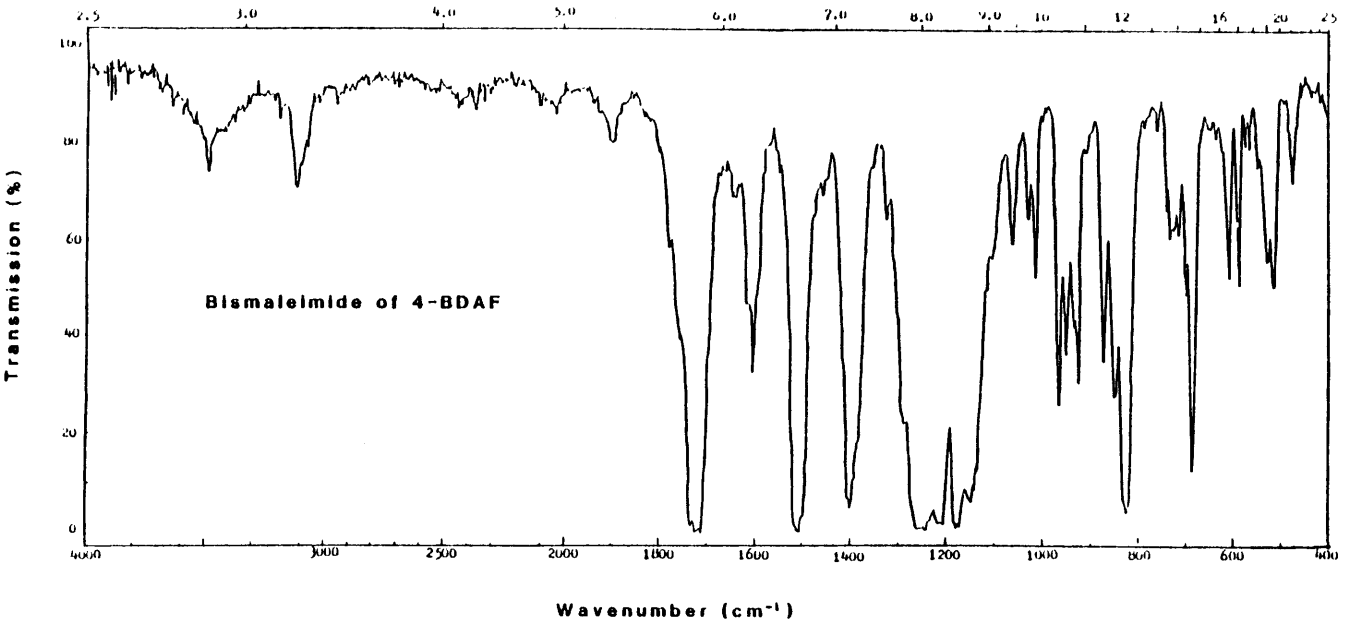
APPENDIX



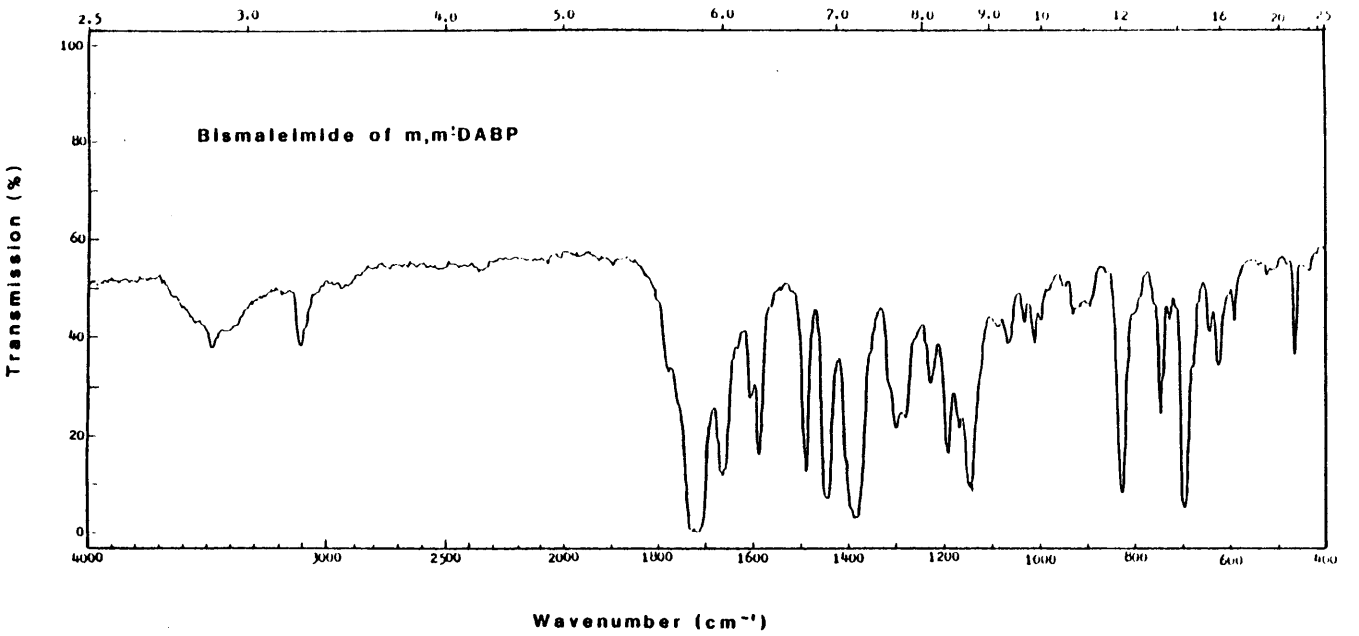
A. Infrared Spectrum of the Oligomer Derived from 4-BDAF/BTDA/NA.



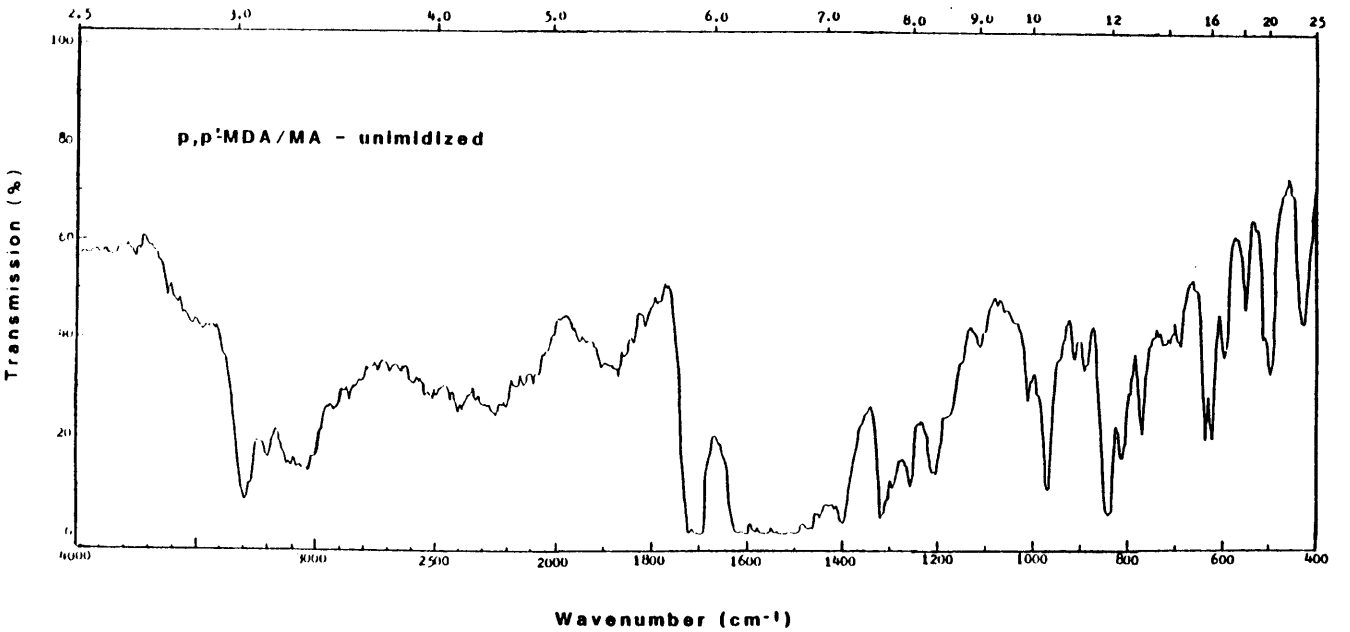
B. Infrared Spectrum of the Unimidized Oligomer Derived from 4-BDAF/BTDA/NA.



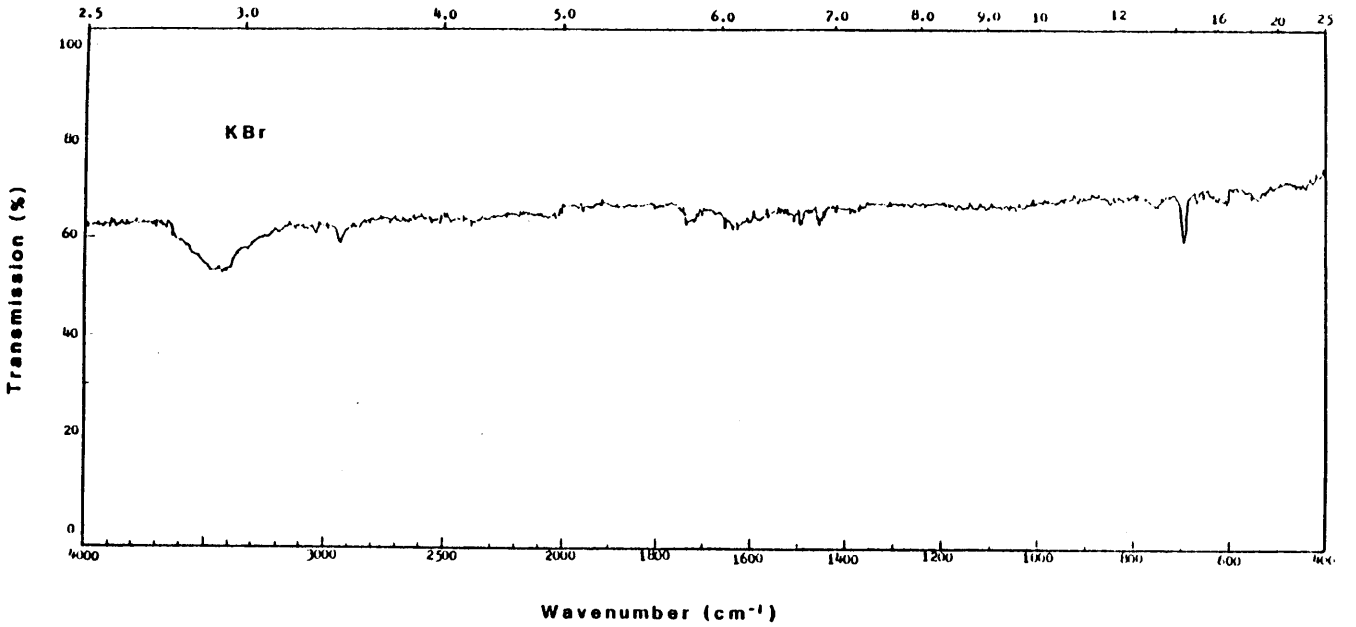
C. Infrared Spectrum of the Bismaleimide of 4-BDAF.



D. Infrared Spectrum of the Bismaleimide of m,m'-DABP.



E. Infrared Spectrum of the Unimidized Oligomer Derived from p,p'MDA and MA.



F. Infrared Spectrum of the KBr.

VITA

Elizabeth Anne Madigan was born on September 18, 1959 in Long Branch, New Jersey. She grew up in Tinton Falls, New Jersey where she graduated in June, 1977, from Monmouth Regional High School. In June, 1982, she received a Bachelor of Science degree (Cum Laude) in Biochemistry from Virginia Polytechnic Institute and State University, Blacksburg, Virginia. While an undergraduate she participated in the Co-operative Education Program offered by the University. As a co-op, she worked for the Food and Drug Administration, Division of Color Technology, Washington, D.C.

In September, 1982, she began her graduate studies toward the Master of Science degree in the Chemistry Department of VPI & SU under the direction of Dr. Larry T. Taylor. Completion of the requirements for the degree of Master of Science was accomplished in March 1984. She married Robert J. Calvey in December, 1983. In April 1984 she assumed a chemist position at the Food and Drug Administration, Washington, D.C.

EMPLOYMENT OF METAL-MODIFIED POLYIMIDES

TO ACHIEVE OPTIMUM CONDUCTANCE AT AN ALUMINUM JOINT

by

Elizabeth A. Madigan

(ABSTRACT)

Earlier research relating to the use of polyimides modified with metal-ion complexes and metal particles indicate that enhanced conductivity and adhesive strength can be achieved.

This research evaluated the employment of metal-modified polyimides to achieve optimum conductance at an aluminum joint. Condensation and addition polyimides were employed. The modification of the polyimides occurred in two ways. The first method involved homogeneous doping of the condensation polyimides with metal-ion complexes. The second modification method involved heterogeneous doping of condensation or addition polyimides with particles of a nickel-aluminum alloy.

The polyimide derived from 4,4'-oxydianiline and 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride and homegeneously or heterogeneously doped was initially employed. Imidization occurred within the aluminum joint. Resistances were measured in the milliohm region, which were too large for the desired application. Therefore, experiments were conducted in an effort to reduce the resistances via use of pre-formed films or powders which have been inserted into the Al joint as gaskets surrounding the Ni-Al alloy powder and heated at various temperatures to form a seal. With this method resistances approaching 10 microohms have been measured. Other studies relating to

this effort, involved powders of various polyimides and different degrees of metal loadings. With 80% of the Al-Ni alloy, resistances between 15 and 40 microohms were achieved.