Electrically Conductive Polyimides Containing Silver Trifluoroacetylacetionate

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Polyimides with enhanced electrical conductivity are produced by adding a silver ion-containing additive to the polyamic acid resin formed by the condensation of an aromatic dianhydride with an aromatic diamine. After thermal treatment the resulting polyimides had surface conductivities in the range of 1.7×10⁻⁴ to 4.5 Ω⁻¹ making them useful in low electronics industry as flexible, electrically conductive polymeric films and coatings.

14 Claims, No Drawings
1 ELECTRICALLY CONDUCTIVE POLYIMIDES CONTAINING SILVER TRIFLUOROACETYLACETONATE

ORIGIN OF THE INVENTION

The invention described herein was jointly made by an employee of the United States Government and contract employees during the performance of work under NASA Contract NAS1-19000 and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, as amended Public Law 85-568 (72 Stat. 435; 42 USC 2457j), and during the performance of work under NASA Grant NAG-1-343. In accordance with 35 USC 202, the grantee elected not to retain title.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates generally to conductive polymers. It relates particularly to aromatic condensation polyimide films and coatings which have surface conductivities in the range of 1.7×10⁻²⁰ to 4.5 Ω⁻¹, and to the process for their preparation.

2. Description of the Related Art

The incorporation of metal salts and complexes has been used as a means of providing polyimides with increased bulk conductivities and/or greatly enhanced surface conductivities. Additives of numerous metals including platinum, palladium, copper, cobalt, gold and silver have been investigated. (L. T. Taylor, et al., U.S. Pat. No. 4,311,615 (1982) and L. T. Taylor, V. C. Carver, T. A. Furtsch, “Incorporation of Metal Ions into Polyimides,” ACS Symposium Series. No. 121 Modification of Polymers, C. E. Carrrher, Jr., and M. Tsuda, Eds., pp 71–82, 1980.) Polymides with metallized silver surfaces have been reported with the addition of silver acetate and silver nitrate to the polyamic acid resin (A. L. Endrey and E. I. De Pont De Nemours and Co., U.S. Pat. No. 3,073,784 (1963) and A. Auerbach, J. Electrochem. Soc., p. 957, April 1984.). Conductive surfaces were achieved after extended cure times or a high temperature (360–370°C.) bake under a blanket of carbon powder. In addition to the incorporation of silver acetate or nitrate into polyamic acid resins as a polyamic acid resin containing silver trifluoroacetylace- tonate.

3. Description of the Preferred Embodiments

Preparation of polyimide films and coatings according to the present invention involves the room temperature reaction in a solvent of an aromatic diamine with an aromatic dianhydride to yield a polyamic acid resin. This polyamic acid resin is then cast as a film and thermally cured, preferably at 250–300°C. to give a polyimide film. Examples of suitable solvents are N,N-dimethylacetamide, N,N-dimethylformamide, N-methyl-2-pyrrolidone, dimethlysulfoxide, and bis(2-methoxyethyl)ether.

The polyamic acids of this invention involve the addition of an equimolar quantity of an aromatic dianhydride such as 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) or pyromellitic dianhydride (PMDA) to a stirred solution of an aromatic diamine such as 4,4'-oxydianiline (4,4'-ODA) or 2,2'-[(4-aminophenoxy)phenyl] hexafluoropropionate (4-BDAP) in an amide-type solvent. Although BTDA and PMDA were used for the specific examples, other dianhydrides can be employed such as 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide diahydride (BDDS), 2,2'-bis(3,4-dicarboxyphenoxy)hexafluoropropionate dianhydride (6FDA), 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride, and 3,4,3',4'-biphenyl tetracarboxylic dianhydride. These diamines which were used in the specific examples were 4,4'-ODA and 4-BDAP; however other diamines also useful in the present invention include any isomer of oxadiazilene, dianmonobenzophenone, dianmonophenylmethane, phenylenediamine, dianmonophenylsulone and bis(aminophenoxy)phenyl hexafluoropropionate.

In addition to polyamic acid resins obtained by reacting equimolar amounts of aromatic diamine and dianhydride, endcapped polyamic acid resins are also useful in the present invention. They are obtained by adding an excess of BTDA, phthalic anhydride (PA) or other anhydride or dianhydride to the polyamic acid resin.

According to the present invention, the incorporation of silver trifluoroacetylace- tonate into the polyamic acid resin was found to provide a means of increasing the surface conductivity of the thermally cured aromatic condensation polyimide. This silver complex can be added immediately
resin is enhanced by the addition of a small amount of silver trifluoroacetylacetonate before its addition to the polyamic acid resin.

Although, the most successful combination of film flexibility and conductivity has been obtained using a 1:1,1:1.74 or a 1:2 mole ratio of silver trifluoroacetylacetonate to polyimide repeat unit, higher and lower concentrations may be used with differing heating schedules to achieve highly satisfactory silver metallized films.

**SPECIFIC EXAMPLES**

**Example 1**

3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA)/4,4'-oxydianiline (4,4'-ODA) resin endcapped with 2% BTDA was prepared by reacting 4.005 g (0.0200 moles) 4,4'-ODA with 6.572 g (0.0204 moles) BTDA in 56.2 g N,N-dimethylacetamide (DMAc). To 4.5424 g of this resin was added 0.2194 g (0.082 mmol) silver trifluoroacetylacetonate (Agtfa) in 2.0 ml of DMAc. After stirring for 1.5 hours a film was cast onto a soda-lime glass plate to a wet thickness of 0.019". The silver ion-containing polyamic acid film was thermally converted to the corresponding surface conducting polyimide by successive one hour heatings in a forced air oven at 100°, 200° and 300° C. The resulting flexible, reflective film had surface conductivity by four point probe.

**Example 2**

BTDA/4,4'-ODA resin endcapped with 2% phthalic anhydride (PA) was prepared by reacting 4.005 g (0.0200 moles) 4,4'-ODA with 6.381 g (0.0200 moles) BTDA and 0.0593 (0.0004 moles) PA in 42.2 g DMAc. To 34.522 g of this resin was added 1.9546 g (0.0200 moles) BTDA and 0.0593 g Agtfa in 30 ml (28.1 g) DMAc. After stirring for 2 hours a film was cast 0.019" thick on a glass plate. The silver ion-containing polyamic acid film was thermally converted to the corresponding surface conducting polyimide by heating in a preheated forced air oven for 20 min at 80° C, 1 hour at 100°, 1 hour at 200° and 2 hours at 300° C. The resulting flexible, reflective film had a conductivity of 1.5 Ω⁻¹ by four point probe.

**Example 3**

BTDA/4,4'-ODA resin was prepared by reacting 10.012 g (0.050 moles) 4,4'-ODA with 16.081 g (0.050 moles) BTDA in 149.9 g DMAc. To 5.039 g of this resin was added 0.215 g Agtfa in 1.182 g DMAc. After stirring for approximately 2 hours a film was cast 0.018" thick on a glass plate. The silver ion-containing polyamic acid film was thermally converted to the corresponding surface conducting polyimide by heating for 1 hour at 100°, 1 hour at 200° and 4 hours at 300° C. The resulting flexible, reflective film had an average conductivity of <4.53Ω⁻¹ by four point probe.

**Example 4**

PMDA/4,4'-ODA resin was prepared by reacting 16.019 g (0.080 moles) of 4,4'-ODA with 17.450 g (0.080 moles) of PMDA in 189.7 g DMAc. To 10.004 g of this resin was added 0.521 g Agtfa in 1.996 g DMAc. The mixture was stirred vigorously with a metal spatula and cast 0.018" thick on a glass plate. The silver ion-containing polyamic acid film was thermally converted to the corresponding surface conducting polyimide by heating for 1 hour each at 100°, 200°, and 300° C and postcuring 2 hours at 300° C. The resulting flexible, reflective film had a conductivity of 1.7×10⁻³–6.2×10⁻³ Ω⁻¹ by four point probe.

**Example 5**

A 15% solids solution of BTDA/4-BDAF polyamic acid was prepared by dissolving 25.9445 g (0.050 moles) of 4-BDAF in 238.2 g of DMAc, and then adding 16.1085 g (0.050 moles) BTDA. To 40.0262 g of this polyamic acid resin was added 1.9374 g of Agtfa in 8.0108 g of DMAc. The solution was stirred vigorously with a metal spatula and immediately cast on plate glass. The silver ion doped polyamic acid resin was converted to the surface-conducting polyimide by curing in a forced air oven 1 hr each at 100° and 200° C, and 3 hr at 300° C. The average conductivity of the air side was 4.5 Ω⁻¹ by four point probe.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A process for producing linear aromatic polyimide films and coatings having surface conductivity comprising: forming a polyamic acid solution by chemically reacting equimolar quantities of an aromatic diamine and an aromatic dianhydride in a solvent medium; adding silver trifuluoroacetylacetonate in a solvent medium to the polyamic acid solution; applying a film layer of the polyamic acid solution containing the silver trifuluoroacetylacetonate onto a surface; and thermally curing the applied film layer to yield a metallized surface conductive polyimide film.

2. The process of claim 1, wherein endcapping of the polyamic acid is effected before the film layer is applied onto the surface.

3. A process for producing linear aromatic polyimide films and coatings having surface conductivity comprising: preparing a solution of an aromatic diamine in a solvent medium and adding thereto an equimolar quantity of an aromatic dianhydride followed by silver trifuluoroacetylacetonate in a solvent medium to provide a reaction mixture; chemically reacting the aromatic diamine and the aromatic dianhydride in the reaction mixture to form a solution of a polyamic acid containing silver trifuorooctacetylacetonate; applying a film layer of the solution of the polyamic acid containing silver trifuorooctacetylacetonate onto a surface; and thermally curing the applied film layer to yield a metallized surface conductive polyimide film.

4. The process of claim 1, wherein endcapping of the polyamic acid is effected before the film layer is applied onto the surface.

5. The process of claim 1, wherein silver trifuorooctacetylacetonate is added in an amount sufficient to provide a molar concentration of silver trifuorooctacetylacetonate to polyimide repeat unit of from about 1:1 to about 1:2.

6. The process of claim 3, wherein silver trifuorooctacetylacetonate is added in an amount sufficient to provide a molar concentration of silver trifuorooctacetylacetonate to polyimide repeat unit of from about 1:1 to about 1:2.

7. The process of claim 1, wherein the aromatic diamine is selected from the group consisting of 4,4'-oxydianiline and 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane.
8. The process of claim 3, wherein the aromatic diamine is selected from the group consisting of 4,4'-oxydianiline and 2,2-bis[4-(4-aminophenoxy) phenyl]hexafluoropropane.

9. The process of claim 1, wherein the aromatic dianhydride is selected from the group consisting of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and pyromellitic dianhydride.

10. The process of claim 3, wherein the aromatic dianhydride is selected from the group consisting of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and pyromellitic dianhydride.

11. The process of claim 2, wherein encapping is effected by means of an encapper selected from the group consisting of 3,3'-4,4'-benzophenone tetracarboxylic dianhydride and phthalic anhydride.

12. The process of claim 4, wherein encapping is effected by means of an encapper selected from the group consisting of 3,3'-4,4'-benzophenone tetracarboxylic dianhydride and phthalic anhydride.

13. The process of claim 1, wherein the solvent medium is selected from the group consisting of:

N, N-dimethylacetamide,
N, N-dimethylformamide,
N,-methyl-2-pyrrolidone,
dimethylsulfoxide and bis(2-methoxyethyl) ether.

14. The process of claim 3, wherein the solvent is selected from the group consisting of:

N, N-dimethylacetamide,
N, N-dimethylformamide,
N,-methyl-2-pyrrolidone,
dimethylsulfoxide and bis(2-methoxyethyl) ether.

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