ELECTRICALLY CONDUCTIVE POLYMIDES CONTAINING SILVER TRIFLUOROACETYLACETONATE

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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 the electronics industry as flexible, electrically conductive polymeric films and coatings.

14 Claims, No Drawings
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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 2457), 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 reproducibility in conductivity, (2) high cost, and (3) inability to produce large-scale quantities of material.

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. Fursts, "Incorporation of Metal Ions into Polyimides", ACS Symposium Series. No. 121 Modification of Polymers, C. E. Carrher, Jr., and M. Tsuda, Eds., pp 71-82, 1980.) Polyimides 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. DuPont De Nemours and Co., U.S. Pat. No. 3,073,784 (1963) and A. Aserbach, J. Electrochem. Soc., p. 937, April 1984.). Conductive surfaces were achieved after extended cure times or a high temperature (360° C.-370° C.) bake under a blanket of carbon powder. In addition to the incorporation of silver acetate or nitrate into polyamic acid resins as diaminodiphenylsulfone and 2,2'-[4-(4-aminophenoxy)phenylene]hexafluoropropane, silver trifluoroacetylacetonate can be added immediately as a polyamic acid resin containing silver trifluoroacetylacetonate.

By the present invention, aromatic condensation polyimide films and coatings are produced which have surface conductivities that have been increased by the incorporation of silver trifluoroacetylacetonate. Provided are materials that are electrically conducting in the range that is useful for films and coatings for the electronics industry, where the combination of conductivity, mechanical stability and thermal stability are required.

The novel conducting polyimide compositions of the present invention are a significant improvement over the prior art. Conducting films according to the present invention are achieved by using a lower cure temperature. In addition, the method of the present invention eliminates altogether the need for a cumbersome blanket of carbon powder used in prior art methods to effect conductivity. The method of the present invention is also superior to the prior art method of counter-current diffusion, because of the handicaps of the latter process which include (1) a lack of reproducibility in conductivity, (2) high cost, and (3) inability to produce large-scale quantities of material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preparation of polyimide films and coatings according to the present invention involves the following steps: a) preparing a solution of polyamic acid resin containing silver trifluoroacetylacetonate; b) immersing the solution into a polyamic acid resin containing silver trifluoroacetylacetonate; c) allowing the solution to precipitate; and d) drying the solution.

The polyamides of this invention involve the addition of an equimolar quantity of an aromatic diamine with a polyamic acid resin obtained by reacting aromatic diamine such as 4,4'-oxydianiline (4,4'-ODA) or 2,2'[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAP) in an amide-type solvent. Although 4-BDAP and 4,4'-ODA were used for the specific examples, other diamydrines can be employed such as 4,4'-oxiphthalic anhydride (OPDA), 4,4'-bis(3,4-dicarboxyphenoxy) diphenylsulfide dihydride (BDSDA), 4,4'-bis(3,4-dicarboxyphenoxy)hexafluoropropene dihydride (6FDA), 1,4-bis(3,4-dicarboxyphenoxy)benzene dihydride, and 3,3',4,4'- bipolar tetrahydroxy dihydride. The dihydrides that 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 oxadialine, diaminobenzophenone, diaminophenylmethane, phenyldenediimine, diaminodiphenylsulfone and bis(aminophenoxy)phenyl hexafluoropropene.

In addition to polyamic acid resins obtained by reacting equimolar amounts of aromatic diamine and dihydride, 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 dihydride to the polyamic acid resin.

According to the present invention, the incorporation of silver trifluoroacetylacetonate 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...
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following the dihydride, or after the polyamic acid polymerization is complete. The solubility of the additive in the resin is enhanced by the addition of a small amount of solvent to the 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 1:1:1.74 or a 1:2 molar 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'-Benzenophone tetracarboxylic dihydride (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 (0.782 mmoles) silver trifluoroacetylacetonate (Agtfa) in 2.0 ml of DMAc. After stirring for 1½ 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 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 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 g (0.0004 moles) PA in 42.2 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 \( \Omega^{-1} \) by four point probe.

Example 3

BTDA/4,4'-ODA resin 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 each at 100°, 1 hour at 200° and 4 hours at 300° C. The resulting flexible, reflective film had an average conductivity of \(<4.5\Omega^{-1}\) 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} \( \Omega^{-1} \) by four point probe.

Example 5

A 15% solids solution of BTDA/4,4'-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 \( \Omega^{-1} \) 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 diimide and an aromatic dihydride in a solvent medium; adding silver trifluoroacetylacetonate in a solvent medium to the polyamic acid solution; applying a film layer of the polyamic acid solution containing the silver trifluoroacetylacetonate 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 diimide in a solvent medium and adding thereto an equimolar quantity of an aromatic dihydride followed by silver trifluoroacetylacetonate in a solvent medium to provide a reaction mixture; chemically reacting the aromatic diimide and the aromatic dihydride in the reaction mixture to form a solution of a polyamic acid containing silver trifluoroacetylacetonate; applying a film layer of the solution of the polyamic acid containing silver trifluoroacetylacetonate onto a surface; and thermally curing the applied film layer to yield a metallized surface conductive polyimide film.

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

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

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

7. The process of claim 1, wherein the aromatic diimide is selected from the group consisting of 4,4'-oxydianiline and 2,2-bis(4-(4-aminophenoxy)pheny1)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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