PATENT SPECIFICATION

(11) **1 590 464**

1 590 464

(21) Application No. 46605/77 (22) Filed 9 Nov. 1977
(31) Convention Application No. 2651194
(32) Filed 10 Nov. 1976 in
(33) Federal Republic of Germany (DE)
(44) Complete Specification published 3 June 1981
(51) INT CL^3 C08L 79/08 C08J 3/02
(52) Index at acceptance
C3R 22C 22D1A1 22D1B3 22D2B1 22D2BX 22N3 C11 C12 C13M C14A C14B C16 C21 C22 C29 C33A C33B C8P C9N L2X L3A L6A L6B L6G LC
C3Y B405 F210 G140

(19)

(54) AQUEOUS POLYIMIDE DISPERSIONS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:—

The present invention relates to aqueous polyimide dispersions, and to their manufacture and their use.

The manufacture of polyimide intermediates (polyamide-acids) from aromatic tetracarboxylic acid anhydrides and aromatic diamines in polar organic solvents is disclosed in German Published Application DAS 1,420,706. Such solutions can be used as wire enamels or as coating agents. On baking, water is eliminated and polyimides having excellent thermal, electrical and mechanical properties are formed. However, on baking, a very large amount of solvents or of their decomposition products is discharged into the environment, causing severe pullution.

It has also been disclosed (in German Laid-Open Applications DOS 2,439,386 and DOS 2,542,866) to prepare aqueous solutions of polyimides from butanetetracarboxylic acid and aromatic diamines. Solubility in water is in this case achieved by reacting the free carboxyl groups with ammonia. On baking, the ammonia is eliminated again and combusted, producing nitric oxides which are serious environmental hazards.

It would be desirable to provide aqueous polyimide dispersions which have particularly advantageous processing characteristics, do not pollute the environment when they are processed, and, when used, display advantageous properties.

According to the present invention, there is provided an aqueous polyimide dispersion which contains from 20 to 60 per cent by weight of a linear polyimide having a particle diameter of less than 5 μm and from 1 to 6 per cent by weight, based on polyimide, of a protective colloid which can be diluted with water, the linear polyimide being a condensation product comprising

(A) from 45 to 55 mole % of condensed units of one or more aromatic diamines,

(B) from 45 to 55 mole % of condensed units of hexanetetracarboxylic acid, pentanetetracarboxylic acid and/or butanetetracarboxylic acid or their derivatives and

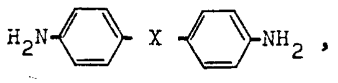
(C) from 0 to 10 mole % of condensed units of an aromatic tetracarboxylic acid or its derivative. According to another aspect of the invention, there is provided a process for the manufacture of an aqueous polyimide dispersion according to the invention, wherein the linear polyimide is first milled dry and is then milled wet using a dispersing mill which generates a high local energy density, the protective colloid being added before milling or during milling.

In a further process, for the manufacture of an aqueous polyimide dispersion according to the invention, a solution of the linear polyimide in a cyclic ether is precipitated in water, with addition of the protective colloid, and the cyclic ether is removed.

These aqueous polyimide dispersions can be used as wire enamels and for the production of heat-resistant impregnations and adhesive assemblies.

The following is to be noted in respect of the components from which the linear polyimides, to be used in the aqueous dispersions according to the invention, are built up.

(A) Examples of aromatic diamines are p-phenylenediamine, m-phenylenediamine and diamines of the general formula



where X is —CH_2—, —O—, —CO—, —SO_2— or —SO—, e.g. 4,4,'-diaminodiphenylmethane, 4,4'-diaminobenzophenone, 4,4'-diaminodiphenyl ether and 4,4'-diaminodiphenyl sulfone or sulfoxide. 4,4'-Diaminodiphenylmethane is particularly preferred as component (A).

The amount of component (A) present as condensed units in the polyimide is from 45 to 55 mole %, preferably from 47.5 to 52.5 mole %.

(B) The component (B) is selected from the aliphatic tetracarboxylic acids hexanetetracarboxylic acid, pentanetetracarboxylic acid and butanetetracarboxylic acid and their derivatives. Butanetetracarboxylic acid is preferred.

The amount of component (B) present as condensed units in the polyimide is from 45 to 55 mole %, preferably from 47.5 to 52.5 mole %.

(C) In addition, up to 10 mole % of an aromatic tetracarboxylic acid or a derivative thereof may be present as condensed units in the polyimide. Examples of aromatic tetracarboxylic acids are pyromellitic acid, 3,3',4,4'-benzophenonetetracarboxylic acid or 3,3',4,4'-diphenylsulfonetetracarboxylic acid.

The polyimides can be manufactured by various processes. Preferably, the tetracarboxylic acid or a derivative thereof is dissolved in a polyhydric alcohol, e.g. ethylene glycol, propylene glycol or triglycol, or in a mixture of a glycol and water and/or N-methylpyrrolidone, whilst heating to 60—100°C. The diamine is then added and the solvent used is distilled off whilst raising the temperature to 200—220°C. In the course thereof, the viscosity of the resin formed increases, and is determined periodically. The progressive increase in brittleness of the chilled resin is also monitored by taking samples. The condensation is regarded as complete when a viscous resin which can easily be milled on cooling is obtained.

In addition to the butanetetracarboxylic acid, pentanetetracarboxylic acid and/or hexanetetracarboxylic acid, or their derivatives, up to 10 mole % of aromatic tetracarboxylic acid(s) or their derivatives may be employed. These are added at the beginning of the reaction.

Mixtures may also be used in the case of the diamines; these may contain from 10 to 90 mole % of each diamine.

It is apparent therefore that the molar ratio of the acids (B and C) to the diamine will vary within the range from 0.9:1.1 to 1.1:0.9. The desired viscosities are best achieved by employing equimolar amounts.

The solvents used in the manufacture of the resins, e.g. glycols or water, are substantially distilled off; where necessary, from 1 to 10% of solvent may be left in the resin to give better leveling properties.

The polyimides used for the manufacture of the aqueous dispersions are in general polyimide condensates having an inherent viscosity of <0.5 [dl/g] (measured on an 0.5% strength solution in N-methylpyrrolidone at 30°C), preferably <0.3 [dl/g], which are usually produced either in a polyhydric alcohol or in water, with removal of the organic solvent. It was surprising that the resins obtained on the one hand give resilient coatings and on the other hand can easily be converted to an aqueous dispersion by mechanical comminution or by dissolving in a cyclic ether and precipitating in water (containing a protective colloid), with removal of the solvent.

The dispersions can be produced either by comminuting the dry polyimide condensate melt to a particle size of $\leqslant 100$ μm by means of a flaking roll or by spraying in a tower, followed by mechanical milling, for example on an impact-disc mill, pin mill or the like. This milling is followed by dispersing and wet milling.

Wet milling may be carried out in mechanical dispersing devices, e.g. in ball mills, preferably in dispersing machinery employing grinding media and generating a high local energy density, e.g. in stirred ball mills, sand mills, Netzsch mills, planetary ball mills and attrition mills. Preferred grinding media are spherical bodies of, for example, glass, ceramic or a hard abrasion-resistant plastic (e.g. nylon) and have a diameter of from 0.2 to 8, preferably from 0.4 to 5 mm.

From about 6 to 10 hours are usually required to mill the material to the desired particle size. The duration of the milling process depends on the brittleness of the polyimide employed.

The protective colloid which can be diluted with water is added either before milling or during milling.

A second process for the manufacture of a polyimide dispersion according to the invention comprises dissolving the polyimide condensate in a cyclic ether, e.g. tetrahydrofuran and/or dioxane, and then precipitating the condensate in water containing the protective colloid. Thereafter, the solvent is distilled off. The particles obtained are spherical, with a maximum size of 5μm. Finer particles can be obtained by additionally subjecting the dispersion to wet milling.

It is also possible to freeze-dry the solutions in cyclic ethers and disperse the fine powder in water, containing protective colloid, after which the dispersion may or may not be briefly wet-milled.

Examples of protective colloids are polyvinylpyrrolidones, polyvinyl alcohols and copolymers of vinylpyrrolidone and acrylates, the amounts used being from 1 to 6, preferably from 2 to 5, % by weight, based on the polyimide.

Toward the end of the wet milling process, leveling agents and anti-thixotropic agents may also be added, with or without other additives, e.g. pigments, fillers, dyes or catalysts. The dispersions according to the invention contain particles having a diameter of less than 5 μm, preferably of from less than 0.05 to 1.5 μm.

Examples of leveling agents which may be used, in amounts of from 1 to 5 per cent by weight based on polyimide, are N-methylpyrrolidone, butylglycol, triglycol, dimethylacetamide, dimethylformamide and the like.

Examples of anti-thixotropic agents, which may be used in amounts of from 0.5 to 5 per cent by weight, based on polyimide, are ethanolamine, diethanolamine and triethanolamine.

Examples of curing catalysts are titanates or oxo-titanium compounds, e.g. triethanolamine titanate and oxo-titanium oxalates, citrates, lactates, tartrates, salicylates, phthalates, formates and gluconates. These may be employed in amounts of from 0.1 to 5 parts by weight, based on the polycondensate.

The dispersions manufactured according to the invention do not suffer from the disadvantages, described above, of organic or aqueous surface-coating solutions. They do not necessitate the additional expenditure on equipment which pulverulent systems generally entail, and may be applied by conventional methods, e.g. spraying, dipping, casting, flooding, impregnating, brushing or knife-coating. The dispersions manufactured according to the invention give high-quality heat-resistant wire enamels, impregnations, adhesive assemblies, laminates, composite materials and prepregs. It was not foreseeable that the properties of enameled wires, laminates, prepregs, impregnations and adhesive assemblies obtained with the dispersions manufactured according to the invention would at least match the properties of coatings applied from solution.

In the Examples, parts and percentages are by weight, unless stated otherwise.

EXAMPLE 1

40 parts of 1,2,3,4-butanetetracarboxylic acid dianhydride were dissolved in 80 parts of ethylene glycol by heating to 80°C. 40 parts of 4,4'-diaminodiphenylmethane were then added. The temperature was raised to 200°C. After a reaction time of 3 hours, 81 parts of ethylene glycol and water were distilled off. A homogeneous resin having an inherent viscosity of 0.14 [dl/g] (measured on an 0.5% strength solution in N-methylpyrrolidone at 30°C) was obtained.

The product was subsequently comminuted by means of an impact-disc mill (n=9,000 rpm; M=5 kg/h) to a mean particle size of 20 μm. To produce 1,000 parts of finished dispersion, 300 parts of polyimide powder, 695 parts of water, 3 parts of a copolymer of vinylpyrrolidone and vinyl propionate, 1.5 parts of ethanolamine and 0.5 part of a polyvinyl alcohol having a residual acetate content of 30% were milled in a Dyno laboratory mill to give a dispersion (10 passes, 10 kg of dispersion/h). The maximum particle size was about 2.6 μm.

Copper wires were coated with this dispersion in a wire enamelling machine having a 2.5 m long oven, at 500°C. The enamelled wire was found to have the following properties, at a coating thickness of 25 μm.

increase in diameter (wire diameter 0.8 mm)	50 μm
breakdown voltage	7.5 kV
heat shock resistance, 300°C×1 hour, 1 diameter	satisfactory
pencil hardness	5H
softening point	380°C
winding about its own diameter, after 15% prestretch	satisfactory

EXAMPLE 2

468 parts (2.0 moles) of 1,2,3,4-butanetetracarboxylic acid, 396 parts (2.0 moles) of 4,4′-diaminodiphenylmethane, 160 parts of triethylene glycol and 800 parts of water were introduced into a 3 l four-necked flask. The mixture was heated whilst stirring. After carrying out the reaction for 7 hours at 100—130°C, 860 parts of water had distilled off. A resin having an inherent viscosity of 0.16 [dl/g] (measured on an 0.5% strength solution in N-methylpyrrolidone at 30°C) was obtained. The brittle resin was then converted to a dispersion as described in Example 1. Copper wires were enamelled with the dispersion, by the method described in Example 1; these wires had the same properties as those specified in Example 1.

EXAMPLE 3

234 parts (1.0 mole) of 1,2,3,4-butanetetracarboxylic acid, 200 parts (1.0 mole) of 4,4′-diaminodiphenyl ether, 80 parts of ethylene glycol and 400 parts of water were introduced into a 2 l four-necked flask. The mixture was heated to 100°C whilst stirring. After carrying out the reaction for 7 hours at 110—130°C, 430 parts of water had distilled off. A resin having an inherent viscosity of 0.22 [dl/g] (measured on an 0.5% strength solution in N-methylpyrrolidone at 30°C) was obtained.

The resin was dissolved in 600 parts of tetrahydrofuran at 80—90°C, and the solution was cooled to room temperature and dispersed, with vigorous stirring, in 800 parts of water, in which 5% of a protective colloid based on polyvinyl alcohol, with 30 mole % of residual acetate, had been dissolved. Thereafter, 590 parts of tetrahydrofuran were distilled off.

Glass mats were impregnated with the dispersion and the water was removed until a resin content of 35 per cent by weight was reached. 16 layers of the glass fiber-reinforced prepregs were stacked and pressed at 350°C under a pressure of 350 kp.cm^{-2} to give laminates. These laminates had a flexural strength of 3,150 kp.cm^{-2}.

WHAT WE CLAIM IS:—

1. An aqueous polyimide dispersion which contains from 20 to 60 percent by weight of a linear polyimide having a particle diameter of less than 5 μm and from 1 to 6 per cent by weight, based on polyimide, of a protective colloid which can be diluted with water, the linear polyimide being a condensation product comprising

(A) from 45 to 55 mole % of condensed units of one or more aromatic diamines,

(B) from 45 to 55 mole % of condensed units of hexanetetracarboxylic acid, pentanetetracarboxylic acid and/or butanetetracarboxylic acid or their derivatives, and

(C) from 0 to 10 mole % of condensed units of an aromatic tetracarboxylic acid or its derivative.

2. An aqueous polyimide dispersion as claimed in claim 1, wherein component (A) is 4,4′-diaminodiphenylmethane.

3. An aqueous polyimide dispersion as claimed in claim 1 or 2, wherein component (B) is butanetetracarboxylic acid.

4. An aqueous polyimide dispersion as claimed in any of claims 1 to 3, wherein the protective colloid which can be diluted with water is polyvinylpyrrolidone, a copolymer of vinylpyrrolidone with a vinyl ester and/or an acrylic ester, and/or polyvinyl alcohol.

5. An aqueous polyimide dispersion as claimed in claim 1 substantially as described in any of the foregoing Examples.

6. A process for the manufacture of an aqueous polyimide dispersion as claimed in claim 1, wherein the linear polyimide is first milled dry and then milled wet using a dispersing mill generating a high local energy density, the protective colloid being added before milling or during milling.

7. A process for the manufacture of an aqueous polyimide dispersion as claimed in claim 1, wherein a solution of the linear polyimide in a cyclic ether is

precipitated in water, with addition of the protective colloid, and the cyclic ether is removed.

8. An aqueous polyimide dispersion when manufactured by a process as claimed in claim 6 or 7.

9. Use of an aqueous polyimide dispersion as claimed in any of claims 1 to 5 or 8 as a wire enamel.

10. Use of a aqueous polyimide dispersion as claimed in any of claims 1 to 5 or 8 as heat-resistant impregnations and adhesives.

11. Metal wires coated with an aqueous polyimide dispersion as claimed in any of claims 1 to 5 or 8 and baked to form an enamel.

12. Laminates, composite materials, impregnations or adhesive assemblies incorporating a polyimide resin applied from a dispersion as claimed in any of claims 1 to 5 or 8.

J. Y. & G. W. JOHNSON,
Furnival House,
14—18 High Holborn,
London, WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1981
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.