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(54) AQUEOUS POLYAMIDE/IMIDE 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 polyamide-imide dispersions, their manufacture and their use.

The manufacture of polyamide-imides from trimellitic anhydride-chloride and diamines is disclosed in German Published Application DAS 1,520,968. In this process, hydrochloric acid, which can only be removed with difficulty, is formed in the course of the reaction.

The reaction of trimellitic anhydride with isocyanates has also been disclosed (German Laid-Open Application DOS 1,595,797). This reaction must be carried out with exclusion of water, since the reaction of isocyanates with water forms amines which in turn can react with isocyanates to give polyureas, which are known to have poor thermal properties. The use of polyamide-imide solutions in organic solvents, obtained by these processes, for wire enamelling causes severe pollution of the environment.

The manufacture of polyamide-imides from butanetetracarboxylic acid, organic diamines and trimellitic anhydride in aqueous solutions has also been disclosed (German Laid-Open Applications DOS 2,519,673 and DOS 2,542,866). Solubility in water was achieved by reacting the free carboxyl groups with ammonia. On baking, the ammonia is split off again and combusted, producing nitric oxides which are serious environmental hazards.

It would be desirable to provide aqueous polyamide-imide dispersions which exhibit particularly advantageous processing characteristics, do not pollute the environment when they are processed, and exhibit advantageous properties in use.

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

(A) from 35 to 55 per cent by weight of condensed units of one or more aromatic diamines,

(B) from 10 to 60 percent by weight of condensed units of one or more aromatic tricarboxylic acid anhydrides or their derivatives,

(C) from 5 to 45 percent by weight of condensed units of hexanetetracarboxylic acid, pentanetetracarboxylic acid and/or butanetetracarboxylic acid or their anhydrides, and

(D) from 0 to 20 per cent by weight of condensed units of an aromatic tetracarboxylic acid or its derivatives.

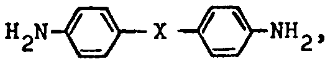
The invention further provides a process for the manufacture of an aqueous polyamide-imide dispersion according to the invention, in which the polyamide-imide is first milled dry and is then milled wet using a dispersing mill which generates a high local energy density, the protective colloid being added before milling or during milling.

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

These aqueous polyamide-imide 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 polyamide-imides, to be used in the aqueous dispersions according to the invention, are built up.

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



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

The amount of component (A) present as condensed units in the polyamide-imide is from 35 to 55 per cent by weight, preferably from 40 to 50 per cent by weight.

(B) Examples of aromatic tricarboxylic acid anhydrides and their derivatives (B) are trimellitic anhydride, 3,4,3' - hemimellitic anhydride, diphenylmethane - 3,3',4 - tricarboxylic acid anhydride, diphenylketone - 3,3' - 4 - tricarboxylic acid anhydride, diphenyl - ether - 3,3',4 - tricarboxylic acid anhydride, diphenylsulfide - 3,3',4 - tricarboxylic acid anhydride, diphenylsulfone - 3,3',4 - tricarboxylic acid anhydride and mixtures of these anhydrides. Esters and partial esters of these tricarboxylic acids, eg. trimellitic acid triglycol ester, diglycol ester or monoglycol ester, may also be used. Trimellitic anhydride is particularly preferred as component (B).

Component (B) is present as condensed units in an amount of from 10 to 60, preferably from 20 to 50, per cent by weight.

(C) Suitable components (C) are the aliphatic tetracarboxylic acids hexanetetracarboxylic acid, pentanetetracarboxylic acid and butanetetracarboxylic acid. 1,2,3,4 - Butanetetracarboxylic acid is preferred.

From 5 to 45, preferably from 10 to 30, per cent by weight of component (C) are present as condensed units in the polyamide-imide.

(D) In addition, up to 20 per cent by weight of an aromatic tetracarboxylic acid or its derivatives may be present as condensed units in the polyamide-imide. Examples of aromatic tetracarboxylic acids are pyromellitic acid, benzophenone - 3,3',4,4' - tetracarboxylic acid and diphenylsulfone - 3,3',4,4' - tetracarboxylic acid.

The polyamide-imides can be manufactured by various processes. Preferably, the tricarboxylic acids and tetracarboxylic acids or their derivatives are dissolved in a polyhydric alcohol, eg. 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 hexanetetracarboxylic acid, or their derivatives, up to 20% by weight 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 typically contain from 10 to 90 mole% of each diamine.

The desired viscosities are best achieved by employing equimolar amounts of diamine(s) and acids.

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

The polyamide-imides used for the manufacture of the aqueous dispersions usually have 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], and 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 a cyclic ether and precipitating in water (containing a protective colloid), with removal of the solvent.

Examples of water-dilutable protective colloids for use in the dispersions are polyvinylpyrrolidones, polyvinyl alcohols and copolymers of vinylpyrrolidone and vinyl propionate and/or copolymers of vinylpyrrolidone and acrylates, the amounts used being from 1 to 6, preferably from 3 to 5, per cent by weight, based on the polyamide-imide.

The dispersions can be produced either by comminuting the dry polyamide-imide condensate melt to a particle size of ≤100μm 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, eg. in ball mills, preferably in dispersing machinery employing grinding media and generating a high local energy density, eg. in stirred ball mills, sandmills, Netzch mills, planetary ball mills and attrition mills. Preferred grinding media are spherical bodies of, for example, glass, ceramic or a hard abrasion-resistant plastic (eg. 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 polyamide-imide employed.

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

A second process for the manufacture of a polyamide-imide dispersion according to the invention comprises dissolving the polyamide-imide condensate in a cyclic ether, eg. 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 5 μm. Finer particles can be obtained by additionally subjecting the dispersion to wet milling.

Toward the end of the wet milling process, leveling agents and anti-thixotropic agents may also be added, with or without other additives, eg. 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 polyamide-imide, are N - methyl - pyrrolidone, butylglycol, triglycol, dimethylacetamide, dimethylformamide and the like.

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

Examples of curing catalysts are titanates or oxo-titanium compounds, eg. 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 solid resin.

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, eg. 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

184.3 parts of trimellitic anhydride, 95 parts of 4,4' - diaminodiphenylmethane, 0.4 part of manganese-II acetate and 800 parts of glycol were introduced into a 3 l four-necked flask provided with a stirrer, a thermometer and a separator. The mixture was then heated whilst stirring. It becomes clear at from 90 to 100°C. At about 140°C, water distils off. After 3 hours at 195—200°C, the melt becomes transparent and 730 parts of glycol are distilled off. The mixture is then cooled to about 150°C. 237.6 parts of 4,4' - diaminodiphenylmethane, 142.5 parts of butanetetracarboxylic acid and 50 parts of glycol are then introduced. The water of reaction distils off in the course of 1 hour at from 100 to 190°C. The temperature is then raised to 195—200°C and a further 50 parts of glycol are distilled off. This produces a viscous resin having an inherent viscosity of 0.133 dl/g (measured on an 0.5% strength solution in N - methylpyrrolidone at 30°C).

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 the polyamide-imide powder formed as described above, 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/h). The maximum particle size was about 3.2 μm.

Copper wires were coated with the dispersion in a wire enameling machine having a 2.5 m long oven, at 500°C (8 passes). A 30 μm thick coating was obtained and the enameled wire was found to have the following properties:

increase in diameter (wire diameter: 0.08 mm)	60 μm
breakdown voltage	4.5 kV
heatshock, 300°C×1 hour, 1×d	satisfactory
pencil hardness	5H
softening point	375°C
winding about its own diameter, after 20% prestretch	satisfactory

EXAMPLE 2

19.2 parts of trimellitic anhydride, 9.9 parts of 4,4' - diaminodiphenylmethane and 62 parts of glycol were introduced into a 3 l four-necked flask equipped with a stirrer, a thermometer and a distillation tube, and the temperature was raised to 180°C whilst stirring and distilling off 38 parts of water and glycol. 33.6 parts of trimellitic anhydride, 8.3 parts of isophthalic acid and 30.0 parts of 4,4' - diaminodiphenylmethane were then added. The temperature was raised to 200°C and 15 parts of glycol were distilled off. The melt was then cooled to 150°C and 24.75 parts of butanetetracarboxylic acid and 24.75 parts of 4,4' - diaminodiphenylmethane were added. After raising the temperature to 200°C, 10 parts of water and glycol were distilled off. After 2 hours, a homogeneous clear melt having an inherent viscosity of 0.18 [dl/g] (measured on an 0.5% strength solution in N - methylpyrrolidone) was obtained.

The melt was converted to a dispersion as described in Example 1. Glass mats were impregnated with the dispersion and cured at 300°C for 5 minutes. Glass fiber-reinforced laminates were then produced from the prepregs at 350°C under a pressure of 150 $kp.cm^{-2}$. These laminates had a flexural strength of 3,600 $kp.cm^{-2}$.

EXAMPLE 3

A viscous resin having an inherent viscosity of 0.189 dl/g (measured on a 0.5% strength solution in N - methylpyrrolidone at 30°C) was obtained, by the method described in Example 1, from 92.2 parts of trimellitic anhydride, 48.5 parts of 4,4' - diaminodiphenyl ether, 0.2 part of manganese-II acetate, 400 parts of glycol, 120 parts of 4,4' - diaminodiphenyl ether and 80.5 parts of butane-1,2,3,4 - tetracarboxylic acid.

The resin was then dissolved in 500 parts of tetrahydrofuran at room temperature. After 2 hours, 400 parts of a 5% strength aqueous solution of a polyvinyl alcohol having a residual acetate content of 30 mole% were added to the resin solution, resulting in a dispersion. 492 parts of tetrahydrofuran were then distilled off whilst raising the temperature to 95°C.

This method of manufacture gives an aqueous dispersion with spherical particles of maximum size 5 μm.

Copper foils were coated with the dispersion; the products had excellent elastic properties. The foils can be used for the manufacture of flexible printed circuits.

WHAT WE CLAIM IS:—

1. An aqueous polyamide-imide dispersion which contains from 20 to 60% by weight of a polyamide-imide having a particle diameter of less than 5 μm and from

1 to 6% by weight, based on polyamide-imide, of a protective colloid which can be diluted with water, the polyamide-imide being a condensation product comprising

(A) from 35 to 55% by weight of condensed units of one or more aromatic diamines,

(B) from 10 to 60% by weight of condensed units of an aromatic tricarboxylic acid anhydride or a derivative thereof,

(C) from 5 to 45% by weight of condensed units of one or more aliphatic tetracarboxylic acid compounds selected from hexanetetracarboxylic acid, pentane-tetracarboxylic acid, butanetetracarboxylic acid and their anhydrides, and

(D) from 0 to 20% by weight of condensed units of an aromatic tetracarboxylic acid or a derivative thereof.

2. An aqueous polyamide-imide dispersion as claimed in claim 1, in which component (A) is 4,4' - diaminodiphenylmethane.

3. An aqueous polyamide-imide dispersion as claimed in claim 1 or 2, in which component (B) is trimellitic anhydride.

4. An aqueous polyamide-imide dispersion as claimed in any of claims 1 to 3, in which component (C) is butanetetracarboxylic acid.

5. An aqueous polyamide-imide dispersion as claimed in any of claims 1 to 4, in which the protective colloid which can be diluted with water is selected from polyvinylpyrrolidone, copolymers of vinyl-pyrrolidone with vinyl esters or acrylic esters, and polyvinyl alcohol.

6. A process for the manufacture of an aqueous polyamide-imide dispersion as claimed in claim 1, in which the polyamide-imide 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 polyamide-imide dispersion as claimed in claim 1, in which a solution of the polyamide-imide in a cyclic ether is precipitated in water, with addition of the protective colloid, and the cyclic ether is removed.

8. A process for the manufacture of an aqueous polyamide-imide dispersion carried out substantially as described in any of the foregoing Examples.

9. An aqueous polyamide-imide dispersion when manufactured by a process as claimed in any of claims 6 to 8.

10. A dispersion as claimed in any of claims 1 to 5 or 9 in which the polyamide-imide contains 35 to 45% by weight of component (a).

11. Use of an aqueous polyamide-imide dispersion as claimed in any of claims 1 to 5, 9 or 10 as a wire enamel.

12. Use of an aqueous polyamide-imide dispersion as claimed in any of claims 1 to 5, or 9 or 10 for the production of heat-resistant impregnations and adhesive assemblies.

13. Metal wires coated with an aqueous polyamide-imide dispersion as desired in any of claims 1 to 5, 9 or 10 and baked to form an enamel.

14. Laminates, composite materials, impregnations or adhesive assemblies incorporating a polyamide-imide resin applied from a dispersion as claimed in any of claims 1 to 5, 9 or 10.

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