A coating composition comprises: (a) a resin solution containing a polyamide-imide resin and a solvent having a urea bond; and (b) a powdered solid lubricant. In general, the coating composition containing a polyamide-imide resin does not raise any concern about reproductive toxicity and has excellent lubrication durability.
COATING COMPOSITION CONTAINING POLYAMIDE-IMIDE RESIN

TECHNICAL FIELD

[0001] The present invention relates to a coating composition containing a polyamide-imide resin.


BACKGROUND ART

[0003] Polyamide-imide resins are resin materials exhibiting excellent heat resistance and mechanical strength. Polyamide-imide resins are therefore used as binder components for coating compositions having lubricating properties.

[0004] Conventionally, polyamide-imide resins have been synthesized using amide-based solvents such as N-methylpyrrolidone (NMP), N-ethylpyrrolidone (NPE), N,N-dimethylacetamide, and N,N-dimethylformamide. This is because amide-based solvents have excellent polyamide-imide resin solubility as well as excellent handleability as solvents.

[0005] However, there is a concern that amide-based solvents have reproductive toxicity, and there is a trend to regulate the use thereof primarily in Europe. Accordingly, there is a need to identify solvents suitable for use in the manufacture of polyamide-imide resins and in subsequent uses of the resulting resins to replace amide-based solvents.


[0008] However, when a polyamide-imide resin composition using γ-butyrolactone as a solvent is used as a binder for a lubricant in that the lubrication durability on a product treated therewith is diminished in comparison to cases in which amide-based solvents are used.

[0009] The present invention was conceived in order to solve the problem described above, and the object of the present invention is to provide a coating composition containing a polyamide-imide resin which does not raise any concern about reproductive toxicity and which has excellent lubrication durability.

DISCLOSURE OF INVENTION

[0010] The present inventors arrived at the present invention as a result of conducting dedicated research in order to achieve the objective described above. That is, the object of the present invention is achieved by a coating composition comprising:

(a) a resin solution containing a polyamide-imide resin and a solvent having a urea bond; and

(b) a powdered solid lubricant.

[0011] The solvent having a urea bond preferably has a structure represented by the following chemical formula (A):

\[
\text{(A)}
\]

(where \( R_1 \) represents a saturated hydrocarbon group having from 1 to 9 carbons and \( n \) represents an integer from 1 to 10), and it is particularly preferable for \( R_1 \) to be a saturated hydrocarbon group having from 1 to 3 carbons and for \( n \) to be an integer from 2 to 5.

[0012] The content of the polyamide-imide resin in the resin solution is for example from 10 to 60% by mass and alternatively from 10 to 50% by mass.

[0013] The polyamide-imide resin is preferably prepared by polymerizing a diisocyanate compound and a trivalent carboxylic acid derivative having an acid anhydride group in a solvent having a urea bond.

[0014] The solid lubricant is preferably at least one type selected from the group consisting of fluorine resins, molybdenum disulfide, and graphite.

[0015] The average primary particle size of the solid lubricant is for example from 0.1 to 20 μm and alternatively from 0.1 to 10 μm.

[0016] The content of the solid lubricant in the total solid is for example from 5 to 90% by mass and alternatively from 10 to 70% by mass.

Effects of Invention

[0017] With the present invention, it is possible to provide a coating composition containing a polyamide-imide resin which has excellent lubrication durability without using an amide-based solvent.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The coating composition of the present invention is a coating composition comprising:

(a) a resin solution containing a polyamide-imide resin and a solvent having a urea bond; and

(b) a solid lubricant.

[0019] The solvent having a urea bond in the present invention is not particularly limited as long as it is a solvent which dissolves the polyamide-imide resin, but the solvent preferably has a structure represented by the following chemical formula (A):
(where R represents a saturated hydrocarbon group having from 1 to 9 carbons and “n” represents an integer from 1 to 10).

[0020] Examples of the saturated hydrocarbon group of \( R_1 \) include straight-chain or branched alkyl groups such as methyl groups, ethyl groups, n-propyl groups, isopropyl groups, n-butyl groups, isobutyl groups, sec-butyl groups, tert-butyl groups, pentyl groups, hexyl groups, and heptyl groups. A saturated hydrocarbon group having from 1 to 3 carbons is particularly preferable.

[0021] “n” represents an integer from 1 to 10, but alternatively an integer from 2 to 5.

[0022] Examples of the solvent having a urea bond used in the present invention include the following compounds:

These solvents may be used alone or as a mixture if necessary.

[0023] The polyamide-imide resin of the present invention is not particularly limited as long as it is a polymer having an amide bond and an imide bond in the molecule, but the polyamide-imide resin can be prepared, for example, by polymerizing a diisocyanate compound and a trivalent carboxylic acid derivative having an acid anhydride group in a solvent having a urea bond.

[0024] Examples of the diisocyanate compound used in the preparation of the polyamide-imide resin include compounds represented by the following chemical formulas:

(where X represents CH₂, CO, SO₂, or O).

A trimellitic acid anhydride is preferable. These trivalent carboxylic acid derivatives having acid anhydride groups may be used alone or as a mixture if necessary.

[0027] The polyamide-imide resin may also be prepared by further adding and polymerizing at least one type of a dicarboxylic acid compound or diol compound and/or a tetravalent carboxylic acid derivative having two acid anhydride groups as polymerization components.

[0028] Examples of the dicarboxylic acid compound used in the preparation of the polyamide-imide resin include aromatic dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, naphthalene dicarboxylic acid, and oxydibenzoxazoic acid and aliphatic dicarboxylic acids such as sebacic acid, glutaric acid, adipic acid, azelaic acid, suberic acid, sebamic acid, decanedioic acid, dodecanedioic acid, and cyclohexane dicarboxylic acid. An adipic acid is preferable from the perspective of the balance of the mechanical properties. These dicarboxylic acid compounds may be used alone or as a mixture if necessary.

[0029] Examples of the diol compound used in the preparation of the polyamide-imide resin include aromatic diol
compounds such as resorcinol, hydroquinones, biphenyl diols, bisphenol A, naphthalene diols, aromatic polycarbonate diols, and derivatives of aromatic polycarbonate diols such as aromatic polycarbonate diol-chloroformic acid diesters and aliphatic diol compounds such as ethylene glycol, 1,4-butanediol, 1,6-hexanediol, aliphatic polycarbonate diols, and derivatives of aliphatic polycarbonate diols such as aliphatic polycarbonate diol-chloroformic acid diesters. It is preferable to copolymerize at least one type of monomer selected from the group consisting of aliphatic polycarbonate diols or derivatives thereof. These diol compounds may be used alone or as a mixture if necessary.

[0030] An aliphatic polycarbonate diol or a derivative thereof has the function of improving the workability and adhesiveness of the coating, and the content in the polyamide-imide resin is preferably from 1 to 50 mol % and particularly preferably from 5 to 30 mol %. When the content of the aliphatic polycarbonate diol or a derivative thereof in the polyamide-imide is within the range described above, it is possible to impart sufficient workability and adhesiveness to the coating. When the content of the aliphatic polycarbonate diol or a derivative thereof exceeds 50 mol %, the solvent resistance tends to be diminished.

[0031] Examples of commercially available aliphatic polycarbonate diols or derivatives thereof include trade names PLACCEL CD-205, 205PL, 205HL, 210, 210PL, 210HL, 220, 220PL, and 220HL produced by Daicel Chemical Industries, Ltd., and these may be used alone or as a mixture if necessary.

[0032] Examples of the tetravalent carboxylic acid derivative having two acid anhydride groups used in the preparation of the polyamide resin include biphenyl tetracarboxylic acid dianhydride, pyromellitic anhydride, oxidiophthalic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, diphenyl sulfone tetracarboxylic acid dianhydride, (hexafluorouracil)phthalic acid dianhydride, and terephthalic acid tetracarboxylic acid dianhydride. These tetravalent carboxylic acid derivatives having two acid anhydride groups may be used alone or as a mixture if necessary.

[0033] In addition to the compounds described above, hydroxythiophosphoric acid, hydroxyphosphonic acid, hydroxybiphenyl carboxylic acid, 1,2-aminothiocarboxylic acid, trimethylamine, trimethylolpropane, gluconic acid, lactic acid, fumaric acid, DL-malic acid, xylitol, D-sorbitol, and DL-alanine may be further added and polymerized as necessary.

[0034] From the perspective of the molecular weight and the degree of crosslinking of the polyamide-imide resin to be produced, the compounded amount of the diisocyanate compound, the tetravalent carboxylic acid derivative having an acid anhydride group, the dicarboxylic acid compound or diol compound, and the tetravalent carboxylic acid derivative having two acid anhydride groups is preferably such that the amount of the diisocyanate compound is from 0.8 to 1 mole, alternatively from 0.95 to 1.08 moles, and further alternatively from 1.0 to 1.08 moles with respect to a total of 1 mole of the tetravalent carboxylic acid derivative having an acid anhydride group and, if present, the tetravalent carboxylic acid derivative having two acid anhydride groups.

[0035] The compounding ratio of the tetravalent carboxylic acid derivative having an acid anhydride group and the dicarboxylic acid is preferably from 0.95:0.05 to 0.5:0.5, alternatively from 0.85:0.15 to 0.6:0.40, and alternatively from 0.75:0.25 to 0.65:0.35 as an equivalence ratio. When the compounding ratio is less than 0.95:0.05, the flexibility of the coating film tends to be diminished, whereas when the compounding ratio exceeds 0.50:0.50, the heat resistance tends to be diminished.

[0036] The polyamide-imide resin of the present invention can be prepared by, but is not limited to, the following methods, for example.

(1) Method of obtaining a polyamide-imide resin by reacting the diisocyanate compound, the tetravalent carboxylic acid derivative having an acid anhydride group, and, if present, the dicarboxylic acid compound or diol compound and the tetracarboxylic acid derivative having two acid anhydride groups all at once;

(2) Method of obtaining a polyamide-imide resin by first reacting the dicarboxylic acid compound or diol compound and an excessive amount of the isocyanate compound to synthesize an oligomer having isocyanate groups at the ends and then adding and reacting the tetravalent carboxylic acid derivative having an acid anhydride group and, if necessary, the tetracarboxylic acid derivative having two acid anhydride groups; and

(3) Method of obtaining a polyamide-imide resin by reacting the isocyanate compound and an excessive amount of the tetracarboxylic acid derivative having an acid anhydride group and, if necessary, the tetracarboxylic acid derivative having two acid anhydride groups to synthesize an oligomer having acids or acid anhydride groups at the ends and then adding and reacting the dicarboxylic compound or diol compound.

[0037] The number-average molecular weight of the polyamide-imide resin of the present invention is for example from 10,000 to 75,000, alternatively from 15,000 to 50,000, and further alternatively from 20,000 to 35,000. When the number-average molecular weight of the polyamide-imide resin is less than 10,000, the strength of the coating film tends to be diminished, whereas when the number-average molecular weight exceeds 75,000, the viscosity of the coating composition increases and the operability at the time of coating is diminished. The number-average molecular weight of the polyamide-imide resin is sampled at the time of the synthesis of the resin and measured with a gel permeation chromatograph (GPC) using the calibration curve of standard polystyrene.

[0038] The resin solution of the present invention is a solution in which a polyamide-imide resin is dissolved in a solvent having a urea bond, and the content of the polyamide-imide resin in the resin solution is preferably from 10 to 60% by mass and particularly preferably from 10 to 50% by mass. When the content of the polyamide-imide resin in the resin solution is within the range described above, it is possible to impart sufficient lubricating properties and abrasion resistance to the coating.

[0039] The powdered solid lubricant of the present invention has the function of improving the slidability of the coating. Examples of solid lubricants include organic microparticles such as fluorine resins, polyolefins, and polynamides and inorganic microparticles such as sulfides, graphite, boron nitride, and metal oxides. Specific examples include polytetrafluoroethylene, tetrafluoroethylene-perfluoroalkyl vinyl ether copolymers, tetrafluoroethylene-hexafluoropropylene copolymers, tetrafluoroethylene-ethylenylene copolymers, polystyrene, polycarbonate, polyamide, molybdenum disulfide, tungsten disulfide, graphite, hexagonal boron nitride, aluminum oxide, and zinc.
oxide. It is preferable to use at least one type selected from the group consisting of fluorine resins, molybdenum disulfide, and graphite.

The average particle diameter of the solid lubricant of the present invention can be measured by observations using an electron microscope or with a laser diffraction and scattering method. The average primary particle diameter of the solid lubricant is preferably from 0.1 to 20 µm and particularly preferably from 0.1 to 10 µm.

The content of the solid lubricant of the present invention in the total solid is preferably from 5 to 90% by mass and particularly preferably from 10 to 70% by mass. When the content of the solid lubricant is within the range described above, it is possible to sufficiently improve the lubricating properties and the lubrication durability of the coating.

The coating composition of the present invention may also contain one or more types of additives such as a UV absorber, a photostabilizer, an antioxidant, a thermal polymerization inhibitor, a leveling agent, an anti-foaming agent, a thickening agent, an anti-settling agent, a pigment (an organic coloration pigment or an inorganic pigment), a coloration dye, an infrared radiation absorber, an optical brightener, a dispersing agent, conductive microparticles, an antistatic agent, an antifoaming agent, a coupling agent, and the like, if necessary, as long as the object of the present invention is not inhibited.

The coating composition of the present invention may be applied with any method. Examples of coating methods that can be used include dipping methods, spincoat methods, flowcoat methods, spraying methods, bar-coating methods, gravure coating methods, roll coating methods, blade coating methods, air knife coating methods, and the like. A thickness of the coating film is not particularly limited, but the thickness is preferably from 1 to 50 µm and more preferably from 5 to 30 µm. After application, the coating film may be dried to remove the solvent and, if necessary, baked.

EXAMPLES

The present invention is described in detail below based on practical examples, but the present invention is not limited to the practical examples.

Practical Example 1

Powdered graphite was added to a polyamide-imide resin solution (produced by Hitachi Chemical Co., Ltd., HPC-3010) in which a polyamide-imide resin dissolved in 1,3-dimethyl-2-imidazolidione (DMI) prepared in DMI, so that the content of the powdered graphite was 50 parts by mass per 100 parts by mass of the polyamide-imide resin, and mixed at room temperature. This mixture was diluted using GB to so that the solid content concentration was 15% by mass to form a coating composition to be used in evaluation tests.

Comparative Example 1

A polyamide-imide resin solution (produced by Hitachi Chemical Co., Ltd., HPC-3010) in which a polyamide-imide resin dissolved in GBL was used, and powdered graphite was added, so that the content of the powdered graphite was 50 parts by mass per 100 parts by mass of the polyamide-imide resin, and mixed at room temperature. This mixture was diluted using GBL to so that the solid content concentration was 15% by mass to form a coating composition to be used in evaluation tests.

Comparative Example 2

A coating composition to be used in evaluation tests was formed in the same manner as in Practical Example 1 with the exception that the powdered graphite was replaced with silica (organosilica sol: DMI solution: solid content of approximately 20% by mass).

Reference Example 1

A polyamide-imide resin solution (produced by Hitachi Chemical Co., Ltd., HPC-5000) in which a polyamide-imide resin was dissolved in N-methylpyrrolidone (NMP) was used, and powdered graphite was added, so that the content of the powdered graphite was 50 parts by mass per 100 parts by mass of the polyamide-imide resin, and mixed at room temperature. This mixture was diluted using NMP so that the solid content concentration was 15% by mass to form a coating composition to be used in evaluation tests.

Coating Method

The resulting coating composition was spray-coated onto a test piece (ring) subjected to sandblasting treatment in advance. After the test piece was dried for 10 minutes at 80°C, the test piece was baked for 30 minutes at 240°C to obtain a test piece for testing.

Evaluation Method

Sliding tests were performed under the following conditions using a block-on-ring tester (LFW-1 tester), and the number of cycles until the coefficient of friction increased substantially was measured. Tests were performed with n=2, and the results are shown in Table 1 as the arithmetic mean thereof.

<table>
<thead>
<tr>
<th>Sliding Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring: SAE 4620 Steel, RC 58-63, 22-28 rms</td>
</tr>
<tr>
<td>Block: SAE 01 Steel, RC 58-63, 4-8 rms</td>
</tr>
<tr>
<td>Sliding environment: immersion in 10W-30 engine oil</td>
</tr>
<tr>
<td>Load: 272 N</td>
</tr>
<tr>
<td>Speed: 72 rpm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test results</td>
</tr>
<tr>
<td>Practical Example 1</td>
</tr>
<tr>
<td>Lubrication durability</td>
</tr>
</tbody>
</table>

As is clear from Table 1, it was ascertained that when the coating composition of Practical Example 1 using 1,3-dimethyl-2-imidazolidione as a solvent is used, the coating composition has excellent lubrication durability equivalent to or better than when N-methylpyrrolidone is used as a solvent. On the other hand, when the coating composition of Comparative Example 1 using GBL as a solvent was used, the lubrication durability was substantially dimin-
ished. When the solid lubricant was changed from powdered graphite to an organo silica sol, the lubrication durability was diminished.

INDUSTRIAL APPLICABILITY

[0057] The coating composition of the present invention can be suitably used in the sliding members of various devices which require excellent slidability and lubrication durability. For example, the coating composition can be used for the surface treatment of crank shafts, slide bearings, pistons, gaskets, gears, door panels, instrument panels, door looks, timing belts, and body seals, glass runs, and weather stripping for sunroofs.

1. A coating composition comprising:
   (a) a resin solution containing a polyamide-imide resin and a solvent having a urea bond; and
   (b) a powdered solid lubricant.

2. The coating composition according to claim 1, wherein the solvent having a urea bond has a structure represented by the following chemical formula (A):

   \[ \text{(A)} \]

where \( R_1 \) represents a saturated hydrocarbon group having from 1 to 9 carbons and “n” represents an integer from 1 to 10.

3. The coating composition according to claim 2, wherein \( R_1 \) is a saturated hydrocarbon group having from 1 to 3 carbons and “n” is an integer from 2 to 5 in the solvent having the structure represented by chemical formula (A).

4. The coating composition according to claim 1, wherein the content of the polyamide-imide resin in the resin solution is from 10 to 60% by mass.

5. The coating composition according to claim 4, wherein the content of the polyamide-imide resin in the resin solution is from 10 to 50% by mass.

6. The coating composition according to claim 1, wherein the polyamide-imide resin is formed by polymerizing a diisocyanate compound and a trivalent carboxylic acid derivative having an acid anhydride group in the solvent having a urea bond.

7. The coating composition according to claim 6, wherein the polyamide-imide resin is formed by reacting the diisocyanate compound, the trivalent carboxylic acid derivative having an acid anhydride group, and a dicarboxylic acid compound or diol compound and a tetracarboxylic acid derivative having two acid anhydride groups simultaneously.

8. The coating composition according to claim 6, wherein the polyamide-imide resin is formed by first reacting a dicarboxylic acid compound or diol compound and an excessive amount of the diisocyanate compound to synthesize an oligomer having isocyanate groups at the ends and then adding and reacting the trivalent carboxylic acid derivative having an acid anhydride group and, optionally a tetracarboxylic acid derivative having two acid anhydride groups.

9. The coating composition according to claim 6, wherein the polyamide-imide resin is formed by reacting the diisocyanate compound and an excessive amount of the trivalent carboxylic acid derivative having an acid anhydride group and, optionally a tetracarboxylic acid derivative having two acid anhydride groups to synthesize an oligomer having acids or acid anhydride end groups and then adding and reacting a dicarboxylic compound or diol compound.

10. The coating composition according to claim 1, wherein the solid lubricant is selected from the group consisting of fluorine resins, molybdenum disulfide, and graphite.

11. The coating composition according to claim 1, wherein an average primary particle diameter of the solid lubricant is from 0.1 to 20 \( \mu \text{m} \).

12. The coating composition according to claim 11, wherein the average primary particle diameter of the solid lubricant is from 0.1 to 10 \( \mu \text{m} \).

13. The coating composition according to claim 1, wherein the content of the solid lubricant in the total solid is from 5 to 90% by mass.

14. The coating composition according to claim 13, wherein the content of the solid lubricant in the total solid is from 10 to 70% by mass.

15. A lubricant comprising the coating composition according to claim 1.

16. A device comprising a surface treatment, wherein the surface treatment comprises the lubricant according to claim 15.

17. The device according to claim 16, selected from the group consisting of crank shafts, slide bearings, pistons, gaskets, gears, door panels, instrument panels, door looks, timing belts, body seals, glass runs, and weather stripping for sunroofs.

* * * * *