

DESCRIPTION

Title of Invention: ELECTRICALLY CONDUCTIVE RESIN COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to an electrically conductive resin composition capable of low-temperature curing and giving a cured product superior in bond strength and electric conductivity.

BACKGROUND ART

[0002]

Electrically conductive resin compositions have been conventionally used for attachments of electric and electronic parts of smartphones, electronic mobile devices, and the like and grounding. With the recent downsizing of electronic parts, the amounts of electrically conductive resin compositions to be applied have been decreasing, and electrically conductive resin compositions have been required to have much superior bond strength and electric conductivity so as to exert their performance even with less resin. Plastics are often used for electronic parts in recent years, and hence curing at low temperature such as about 80°C has been required. Examples of electrically conductive resin compositions that cure at low temperature include those disclosed in JP 2000-230112 A and JP 2017-214548 A.

SUMMARY OF INVENTION

[0003]

In curing at low temperature such as about 80°C, however, insufficient curing may occur because of the shortage of thermal energy required for the reaction, causing the cured product to have deteriorated bond strength or electric conductivity.

[0004]

The present invention has been made in view of the circumstance above, and an object of the present invention is to provide an electrically conductive resin composition capable of low-temperature curing and giving a cured product superior in bond strength and electric conductivity. In addition, the present invention

provides a cured product given by curing the electrically conductive resin composition. The present inventors have conducted intensive studies in order to achieve the objects, and discovered a method for an electrically conductive resin composition superior in bond strength and electric conductivity after low-temperature curing, eventually completing the present invention.

[0005]

The following describes the gist of the present invention.

[1] An electrically conductive resin composition comprising components (A) to (C), wherein the component (C) comprises (C-1) and (C-2), and

the component (A) is an epoxy resin,

the component (B) is an electrically conductive particle,

the component (C) is a polyamine-based latent curing agent,

the (C-1) is a polyamine-based latent curing agent having a softening point of 50 to 129°C, and

the (C-2) is a polyamine-based latent curing agent having a softening point of 130 to 180°C.

[2] The electrically conductive resin composition according to [1] or [2], wherein the component (A) comprises a bisphenol epoxy resin.

[3] The electrically conductive resin composition according to any of [1] to [3], wherein the component (A) comprises (A-1) that is an epoxy resin having two or more epoxy groups in one molecule, and (A-2) that is an epoxy resin having one epoxy group in one molecule.

[4] The electrically conductive resin composition according to any of [1] to [4], wherein the component (B) comprises (B-1) that is a crystalline electrically conductive particle.

[5] The electrically conductive resin composition according to [4], wherein the component (B) comprises the (B-1) that is a crystalline electrically conductive particle and (B-2) that is a noncrystalline electrically conductive particle.

[6] The electrically conductive resin composition according to any of [1] to [5], wherein the component (C) is an aliphatic polyamine-based latent curing agent.

[7] The electrically conductive resin composition according to any of [1] to [6], wherein the component (C) is an adduct-modified polyamine-based latent curing agent.

[8] The electrically conductive resin composition according to any of [1] to [7], wherein the component (C)

comprises only the (C-1) and the (C-2).

[9] The electrically conductive resin composition according to any of [1] to [8], wherein a mass ratio between the (C-1) and the (C-2) is 10:90 to 90:10.

[10] A cured product given by curing the electrically conductive resin composition according to any of [1] to [9].

DESCRIPTION OF EMBODIMENTS

[0006]

The present invention will be described in detail below. In the present specification, the expression "X to Y" is used with the meaning that the numerical values shown in before and after it (X and Y) are included as the lower limit value and upper limit value, and means "X or more and Y or less". In the present specification, the term (meth)acrylic means both acrylic and methacrylic. The expression "A and/or B" means including each of A and B, and a combination of A and B.

[0007]

The present invention relates to an electrically conductive resin composition containing components (A) to (C), wherein the component (C) contains (C-1) and (C-2), and

the component (A) is an epoxy resin,

the component (B) is an electrically conductive particle,

the component (C) is a polyamine-based latent curing agent,

the (C-1) is a polyamine-based latent curing agent having a softening point of 50 to 129°C, and

the (C-2) is a polyamine-based latent curing agent having a softening point of 130 to 180°C.

The electrically conductive resin composition according to the present invention, having such a configuration, gives a cured product superior in bond strength and electric conductivity through low-temperature curing.

[0008]

<Component (A)>

The component (A) to be used in the present invention is an epoxy resin.

[0009]

The component (A) may be solid or liquid without limitation as long as the component (A) is an epoxy resin having one or more epoxy groups in one molecule, but, in terms of superiority in curability and workability, preferably contains an epoxy resin having two or more epoxy groups in one molecule, and particularly preferably is liquid. The upper limit of the number of epoxy groups possessed by the epoxy resin having two or more epoxy groups in one molecule is, for example, four or less, or three or less. Specific examples of the component (A) include: a bisphenol epoxy resin; a hydrogenated bisphenol epoxy resin; an alkylene glycol epoxy resin such as 1,2-butanediol diglycidyl ether, 1,3-butanediol diglycidyl ether, 1,4-butanediol diglycidyl ether, (poly)ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, 2,3-butanediol diglycidyl ether, 1,5-pentanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, neopentyl glycol diglycidyl ether, and 1,4-cyclohexanedimethanol diglycidyl ether; a novolac epoxy resin such as a phenolnovolac epoxy resin and a cresolnovolac epoxy resin; a glycidylamine compound such as N,N-diglycidyl-4-glycidyloxyaniline, 4,4'-methylenebis(N,N-diglycidylaniline), tetraglycidyl-diaminodiphenylmethane, and tetraglycidyl-m-xylylenediamine; and a naphthalene epoxy resin having four glycidyl groups. One of these may be used alone, and alternatively two or more thereof may be used in combination; however, for superiority in electroconductivity, the component (A) preferably contains a bisphenol epoxy resin, and preferably contains a bisphenol epoxy resin having two or more epoxy groups. It should be noted that silane coupling agents mentioned later are not regarded as the component (A) but as optional components.

[0010]

The bisphenol epoxy resin may be any epoxy resin having a bisphenol backbone without limitation, and examples thereof include a bisphenol A epoxy resin, a bisphenol F epoxy resin, a bisphenol S epoxy resin, a bisphenol AD epoxy resin, a urethane-modified bisphenol epoxy resin, a rubber-modified bisphenol epoxy resin, and a polyoxyalkylene-modified bisphenol epoxy resin. One of these may be used alone, and alternatively two or more thereof may be used in combination; however, in terms of superiority in electroconductivity and workability, a bisphenol A epoxy resin and a bisphenol F epoxy resin are preferably used in combination, and it is particularly preferable that the mass ratio between the bisphenol A epoxy resin and the bisphenol F epoxy resin be 25:75 to 75:25 or 35:65 to 65:35. The mass of the bisphenol A epoxy resin may be the same as, or larger or smaller than that of the bisphenol F epoxy resin.

[0011]

Examples of commercially available products of epoxy resin include, but are not limited to, epoxy resin components of: jER828, 1001, 801, 806, 807, YX4000, YX8000, and YX8034 (manufactured by Mitsubishi Chemical Corporation); EPICLON 830 and 850, and EXA-830CRP, EXA-830LVP, EXA-850CRP, and EXA-

835LV (manufactured by DIC Corporation); ADEKA RESIN EP-4100, EP-4000, EP-4000S, EP-4080, EP-4085, EP-4088, EPU-6, EPU-7N, EPR-4023, EPR-1309, and EP-4920 (manufactured by ADEKA Corporation); TEPIK (manufactured by Nissan Chemical Industries, Ltd.); KF-101, KF-1001, KF-105, X-22-163B, and X-22-9002 (manufactured by Shin-Etsu Chemical Co., Ltd.); DENACOL EX 411, 314, 201, 212, and 252 (manufactured by Nagase ChemteX Corporation); DER-331, -332, -334, -431, and -542 (manufactured by The Dow Chemical Company); YH-434, YH-434L, and ST-3000 (manufactured by NIPPON STEEL Chemical & Material Co., Ltd.); RIKARESIN HBE-100 (manufactured by New Japan Chemical Co., Ltd.); Epolite 4000 (manufactured by Kyoeisha Chemical Co., Ltd.); and CUREDUC L-07N (manufactured by SHIKOKU CHEMICALS CORPORATION). One of these may be used alone, and alternatively two or more thereof may be used in combination.

[0012]

It is preferable to use (A-1) that is an epoxy resin having two or more epoxy groups in one molecule and (A-2) that is an epoxy resin having one epoxy group in one molecule for the component (A). Although the reason is not clear, use of the (A-1) and the (A-2) in combination allows not only viscosity adjustment, but also reduction of the contact resistance value, thus successfully giving an electrically conductive resin composition having low viscosity and good electric conductivity. Examples of the (A-2) include, but are not limited to, methyl glycidyl ether, ethyl glycidyl ether, butyl glycidyl ether, isobutyl glycidyl ether, phenyl glycidyl ether, 2-ethylhexyl glycidyl ether, decyl glycidyl ether, stearyl glycidyl ether, allyl glycidyl ether, 2-methyloctyl glycidyl ether, methoxy polyethylene glycol monoglycidyl ether, ethoxy polyethylene glycol monoglycidyl ether, butoxy polyethylene glycol monoglycidyl ether, phenoxy polyethylene glycol monoglycidyl ether, p-tertiary-butylphenyl glycidyl ether, sec-butylphenyl glycidyl ether, n-butylphenyl glycidyl ether, phenylphenol glycidyl ether, cresyl glycidyl ether, dibromocresyl glycidyl ether, and neodecanoic acid glycidyl ester. One of these may be used alone, and alternatively two or more thereof may be used in combination. For superiority in storage stability and electric conductivity, p-tertiary-butylphenyl glycidyl ether and/or neodecanoic acid glycidyl ester are/is preferred. For successfully inhibiting generation of outgas in heating, the boiling point of the (A-2) is preferably 290°C or more. The boiling point of the (A-2) can be 450°C or less, 400°C or less, 350°C or less, or 300°C or less. The boiling point of the (A-2) can be 290°C or more and 450°C or less.

[0013]

Examples of commercially available products of the (A-2) include ED-509S (manufactured by ADEKA Corporation), EPIOL (registered trademark) TB (manufactured by NOF CORPORATION), and CARDURA E10P (manufactured by Momentive Performance Materials, Inc.), but are not limited thereto.

[0014]

In using the (A-1) and the (A-2) in combination, the mass ratio of them is preferably 99:1 to 50:50, further preferably 95:5 to 60:40, and most preferably 90:10 to 70:30. The mass ratio falling within the range of 99:1 to 50:50 makes the electrically conductive resin composition superior in storage stability and electric conductivity.

[0015]

<Component (B)>

The component (B) to be used in the present invention is electrically conductive particles. The component (B) is not limited in terms of the material of the particles and the shape of the particles as long as electric conductivity is developed. For example, appropriate particles can be selected from metal particles composed of one or more selected from metals including gold, silver, copper, nickel, palladium, platinum, tin, and bismuth, alloy particles given by combining multiple metals of them, and particles the surfaces of which are covered with any of the metals as a covering layer. One of these may be used alone, and alternatively two or more thereof may be used in combination; however, for electric conductivity and cost, the component (B) is preferably silver particles or particles the surfaces of which are covered with silver as a covering layer. Examples of the shape of the component (B) include spherical, irregular, flake-like, filamentous (needle-like), and dendritic shapes. These may be used alone, or as a mixture. The component (B) may have been surface-treated with a lubricant. For the lubricant, a saturated fatty acid and/or unsaturated fatty acid can be used. Examples thereof include capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, linolenic acid, linoleic acid, palmitoleic acid, oleic acid, malonic acid, and hexanoic acid, and, for superiority in bond strength and electric conductivity after curing at low temperature, it is preferable for the component (B) to have been untreated or treated with stearic acid or oleic acid. One of those may be used alone, and alternatively two or more thereof may be used in combination.

[0016]

The component (B) preferably contains (B-1) that is crystalline electrically conductive particles. The crystalline electrically conductive particles are those produced by a known production method, and an example thereof is a production method commonly called a reduction method, such as that shown in JP 2014-196527 A, in which an electrically conductive particle is produced by growing one crystal. The crystalline electrically conductive particles are flake-like, thin-piece particles such that every flake has a generally identical thickness overall, being in the shape of a polygonal sheet such as the shape of a triangular sheet, and the surfaces of the flakes are generally smooth. The (B-1) is preferably silver particles for superiority in electric conductivity after curing at low temperature.

[0017]

Examples of commercially available products of the (B-1) include, but are not limited to, N300, M612, M13, M27, and LM1 (manufactured by TOKUSEN KOGYO Co., Ltd.).

[0018]

It is preferable to use the (B-1) that is crystalline electrically conductive particles and (B-2) that is noncrystalline electrically conductive particles in combination for the component (B). The weight ratio in using the (B-1) and the (B-2) in combination is preferably 10:90 to 90:10, further preferably 10:90 to 75:25, and most preferably 15:85 to 50:50. The weight ratio falling within the range of 10:90 to 90:10 makes the electrically conductive resin composition superior in electric conductivity after curing at low temperature. The weight ratio in using the (B-1) and the (B-2) in combination may be 20:80 to 45:55, or 25:75 to 45:55.

[0019]

The shape of the (B-2) is not limited, and examples thereof include, as described above, spherical, irregular, flake-like (scale-like), filamentous (needle-like), and dendritic shapes. One of these may be used alone, and alternatively two or more thereof may be used in combination; however, for superiority in electric conductivity, flake-like and/or spherical electrically conductive particles are preferably contained. For example, the term noncrystalline electrically conductive particles refers to flake-like electrically conductive particles given through a pulverizing process, or electrically conductive particles given by covering the surfaces of organic or inorganic particles each with a film of electrically conductive metal. The (B-2) is preferably silver particles or particles each covered with a film of silver for superiority in electric conductivity after curing at low temperature.

[0020]

The average particle size of the component (B) is preferably in the range of 0.01 to 100 μm , more preferably in the range of 0.1 to 50 μm , further preferably 0.1 to 30 μm , and most preferably 0.3 to 10 μm . Here, the average particle size of the component (B) is a particle size at a cumulative volume percentage of 50% (D50) in grain size distribution determined by a laser diffraction/scattering method.

[0021]

For superiority in electric conductivity, the average particle size of the (B-1) is in the range of 0.01 to 30 μm , more preferably in the range of 0.1 to 20 μm , and most preferably 0.3 to 10 μm . Here, the average particle size of the (B-1) is a particle size at a cumulative volume percentage of 50% (D50) in grain size distribution determined by a laser diffraction/scattering method.

[0022]

The thickness (average thickness, T) of the (B-1) is not limited, and preferably 1 nm or more and less

than 1000 nm, more preferably 10 to 200 nm, further preferably 30 to 150 nm, and particularly preferably 60 to 100 nm for making the cured product much superior in electric conductivity. The thickness of the (B-1) can be checked by using a scanning electron microscope (SEM). More specifically, the thickness can be determined in such a manner that 100 particles are randomly extracted from plate-shaped silver particles, the thickness of each particle is measured, and the mean is determined.

[0023]

The average particle size of the (B-2) is preferably in the range of 0.1 to 50 μm , more preferably in the range of 0.1 to 30 μm , further preferably 0.5 to 20 μm , and most preferably 0.5 to 10 μm . Here, the average particle size of each component is a particle size at a cumulative volume percentage of 50% (D50) in grain size distribution determined by a laser diffraction/scattering method.

[0024]

The amount of the component (B) contained is preferably 50 to 500 parts by mass, further preferably 100 to 400 parts by mass, and most preferably 150 to 350 parts by mass per 100 parts by mass of the component (A). The amount of 50 parts by mass or more results in superior electric conductivity such as a low contact resistance value and a low volume resistivity, and the amount of 500 parts by mass or less makes the electrically conductive resin composition superior in workability.

[0025]

The component (B) is contained preferably in an amount of 40 to 95% by mass, further preferably in an amount of 50 to 90% by mass, and most preferably in an amount of 60 to 85% by mass to the whole of the electrically conductive resin adhesive. The amount falling within the range makes the electrically conductive resin adhesive superior in workability and electric conductivity after curing at low temperature.

[0026]

<Component (C)>

The component (C) to be used in the present invention is a latent curing agent containing (C-1) that is a polyamine-based latent curing agent having a softening point of 50 to 129°C and (C-2) that is a polyamine-based latent curing agent having a softening point of 130 to 180°C. While a curing agent other than the component (C) may be contained as a curing agent to be contained in the electrically conductive resin composition according to the present invention, the total amount of the (C-1) and the (C-2) is preferably 50% by mass or more, and more preferably 80% by mass or more to the amount of the curing agents in terms of electric conductivity and bond strength, and containing only the (C-1) and the (C-2) is most preferable. Softening point in the present

invention is a value determined by a measurement method in accordance with a softening point measurement method in JIS K 7234: 1986.

[0027]

Examples of the latent curing agent include an adduct-modified latent curing agent. Examples of the adduct-modified latent curing agent include, but are not limited to, a reaction product given by reacting an amine compound with an isocyanate compound or urea compound (urea adduct-modified latent curing agent) or a reaction product of an amine compound and an epoxy compound (epoxyamine adduct-modified latent curing agent). Examples of the polyamine structure include aliphatic polyamine and aromatic polyamine, and aliphatic polyamine is preferred in terms of curability. That is, an adduct-modified aliphatic polyamine-based latent curing agent is preferred.

[0028]

The component (C) may be liquid or solid, and is preferably solid in terms of storage stability, and further preferably powder in terms of dispersibility. The average particle size of the powder is preferably in the range of 0.1 to 30 μm , more preferably in the range of 0.5 to 20 μm , and most preferably 1 to 10 μm . Here, the average particle size of the component (C) is a particle size at a cumulative volume percentage of 50% (D50) in grain size distribution determined by a laser diffraction/scattering method.

[0029]

The (C-1) is a polyamine-based latent curing agent having a softening point of 50 to 129°C. The softening point of the (C-1) in the form of powder is preferably 125°C or less for superiority in low-temperature curability, and the softening point is preferably 50°C or more, and more preferably 80°C or more for superiority in storability. That is, the softening point of the (C-1) is preferably 50 to 125°C, and more preferably 80 to 125°C.

[0030]

The (C-2) is a polyamine-based latent curing agent having a softening point of 130 to 180°C. The softening point of the (C-2) in the form of powder is preferably 130°C or more for superiority in electric conductivity, and the softening point is preferably 180°C or less, and more preferably 150°C or less for superiority in low-temperature curability. That is, the softening point of the (C-2) is preferably 130 to 180°C, and further preferably 130 to 150°C.

[0031]

Examples of commercially available products of the component (C) include, but are not limited to, Fujicure FXE-1000, FXR-1020, and FXR-1081 and -1061 (manufactured by T&K TOKA CO., LTD.) for the (C-1). Examples of those for the (C-2) include Fujicure FXE-1030 (manufactured by T&K TOKA CO., LTD.). One of these may be used alone, and alternatively two or more thereof may be used in combination.

[0032]

The amount of the component (C) contained, that is, the total amount of the (C-1) and the (C-2) contained is preferably 1 to 100 parts by mass, further preferably 10 to 50 parts by mass, and most preferably 15 to 40 parts by mass per 100 parts by mass of the component (A). The amount of 1 part by mass or more results in superior low-temperature curability, and the amount of 100 parts by mass or less makes the electrically conductive resin composition superior in storage stability.

[0033]

The weight ratio between the (C-1) and the (C-2) is preferably 10:90 to 90:10, further preferably 15:85 to 85:15, further preferably 20:80 to 80:20, further preferably 20:80 to 60:40, and most preferably 20:80 to 50:50. The weight ratio in the range of 10:90 to 90:10 makes the cured product superior in electric conductivity and bond strength.

[0034]

<Other components>

The electrically conductive resin composition of the present invention preferably contains substantially no organic solvent. If the electrically conductive resin composition contains an organic solvent, dissolution of the component (C) by the organic solvent causes deterioration of the storage stability and the separation of the organic solvent, and an impact on the physical properties is found. The phrase containing substantially no organic solvent means that no organic solvent is intentionally contained as a component to be blended in the electrically conductive resin composition; specifically, the amount of an organic solvent contained to the total amount of the electrically conductive resin composition is 1% by mass or less, preferably 0.5% by mass or less, and further preferably 0.1% by mass or less. The amount of 1% by mass or less does not result in the occurrence of the deterioration of the storage stability and the separation.

[0035]

Examples of the organic solvent include: an aromatic organic solvent such as toluene and xylene; an aliphatic organic solvent such as n-hexane; an alicyclic organic solvent such as cyclohexane, methylcyclohexane, and ethylcyclohexane; a ketone organic solvent such as acetone and methyl ethyl ketone; an alcohol organic solvent such as methanol and ethanol; an ester organic solvent such as ethyl acetate and butyl acetate; a propylene

glycol ether organic solvent such as propylene glycol methyl ether, propylene glycol ethyl ether, and propylene glycol-t-butyl ether; and a fluorine-containing solvent.

[0036]

In addition to the above components, any additive as an optional component may be added to the electrically conductive resin composition of the present invention, as necessary, in a manner without impairing the effects of the present invention; otherwise, no additive may be added. Examples of the additive can include a storage stabilizer, rubber particles, a silane coupling agent, a plasticizer, a filler (other than the component (B)), a tackifier, an organic or inorganic pigment, a rust inhibitor, a defoamer, a dispersing agent, a surfactant, a viscoelasticity modifier, a thickener, and an organometallic complex. It is not necessary to add, for example, an additive other than storage stabilizers and plasticizers to the electrically conductive resin composition of the present invention.

[0037]

The electrically conductive resin composition of the present invention may contain a storage stabilizer. Any storage stabilizer that enhances the storage stability is applicable without limitation. For example, a borate compound, phosphoric acid, an alkyl phosphate, p-toluenesulfonic acid, or methyl p-toluenesulfonate may be blended as a storage stabilizer. Examples of borate compounds include trimethyl borate, triethyl borate, tri-n-propyl borate, triisopropyl borate, tributyl borate, trihexyl borate, tri-n-octyl borate, tris(2-ethylhexyloxy)borane, triphenyl borate, trimethoxyboroxine, and 2,2'-(carbonylbisoxo)bis(1,3,2-dioxaborolane-4,5-dione). A commercially available product and/or synthesized product may be used as a storage stabilizer. Examples of commercially available products of borate compounds include a storage stabilizer component of "CUREDUCT (R) L-07N" (manufactured by SHIKOKU CHEMICALS CORPORATION). Applicable alkyl phosphates are, for example, trimethyl phosphate and tributyl phosphate, but are not limited thereto. One storage stabilizer alone or a mixture of multiple storage stabilizers may be used. In view of storage stability, phosphoric acid, a borate compound, trimethoxyboroxine, and methyl p-toluenesulfonate are preferred. A storage stabilizer dispersed in an epoxy resin or in a plasticizer may be used. In the case that a mixture of a storage stabilizer and an epoxy resin is added in adding a storage stabilizer, the epoxy resin is preferably a bisphenol epoxy resin, and examples of the plasticizer include a phenolic resin. Examples of commercially available products of phenolic resin include a plasticizer component of CUREDUCT L-07N (manufactured by SHIKOKU CHEMICALS CORPORATION).

[0038]

The amount of the storage stabilizer contained is preferably 0.01 to 10 parts by mass, further preferably 0.02 to 7 parts by mass, and further preferably 0.05 to 5 parts by mass per 100 parts by mass of the component

(A). The amount of 0.01 parts by mass or more results in superior storage stability, and the amount of 10 parts by mass or less does not cause inhibition of curing. The amount of the plasticizer contained is preferably 0.01 to 10 parts by mass, further preferably 0.02 to 7 parts by mass, and further preferably 0.05 to 5 parts by mass per 100 parts by mass of the component (A).

[0039]

The electrically conductive resin composition of the present invention may contain a filler (other than the component (B)). Acceptable fillers are inorganic fillers such as alumina powder, calcium carbonate powder, talc powder, silica powder, and fumed silica powder and organic fillers such as rubber particles. Containing rubber particles is preferred because the electrically conductive resin composition is allowed to have superior electroconductivity, although the reason is unclear.

[0040]

A rubber particle in the context of the present invention is a particle including a layer with rubber elasticity. Such a rubber particle may be a particle consisting only of one layer with rubber elasticity, or a core-shell particle, which is a particle of multilayer structure with rubber elasticity, and is preferably a core-shell particle for superiority in volume resistivity. Rubber particles dispersed in advance in an epoxy resin may be used. For example, butadiene rubber, acrylic rubber, silicone rubber, butyl rubber, olefin rubber, styrene rubber, NBR, SBR, IR, and EPR are applicable. One of these may be used alone, and alternatively two or more thereof may be used in combination.

[0041]

The core-shell particle is a microparticle in which a part as a core (nucleus) of the particle and a part as a shell (wall) thereof consist of polymers having different characteristics. In producing preferred powder particles to be used in the present invention, first, core parts are produced by polymerizing a polymerizable monomer. Examples of the polymerizable monomer include: a (meth)acrylate monomer such as n-propyl (meth)acrylate, n-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, and n-decyl (meth)acrylate; an aromatic vinyl compound such as styrene, vinyltoluene, and α -methylstyrene; a vinyl cyanide compound such as acrylonitrile and methacrylonitrile; vinylidene cyanide; 2-hydroxyethyl (meth)acrylate; 3-hydroxybutyl (meth)acrylate; 2-hydroxyethyl fumarate; hydroxybutyl vinyl ether; monobutyl maleate; and butoxyethyl methacrylate, further examples include: a crosslinkable monomer having two or more reactive groups such as ethylene glycol di(meth)acrylate, butylene glycol di(meth)acrylate, trimethylolpropane di(meth)acrylate, trimethylolpropane tri(meth)acrylate, hexanediol di(meth)acrylate, hexanediol tri(meth)acrylate, oligoethylene di(meth)acrylate, and oligoethylene tri(meth)acrylate; an aromatic divinyl monomer such as divinylbenzene; and triallyl trimellitate and triallyl isocyanurate, and one polymerizable monomer or two or more different

polymerizable monomer can be selected from them for use. Next, second polymerization is performed to form shells consisting of a polymer having a melting point equal to or higher than room temperature by further polymerizing a polymerizable monomer on the thus-obtained polymer particles as cores. A polymerizable monomer to be used at that time can be selected for use from the same polymerizable monomers to obtain the cores. Preferred examples of polymerizable monomers to be used as a shell material include a (meth)acrylate with an alkyl group having one to four carbon atoms such as ethyl (meth)acrylate, n-butyl acrylate, methyl methacrylate, and butyl methacrylate.

[0042]

While core-shell particles may be synthesized as described above, otherwise, commercially available ones may be used. Applicable commercially available products of core-shell particles are: PARALOID EXL-2655 (manufactured by Kureha Chemical Industry Co., Ltd.), which consists of butadiene-alkyl methacrylate-styrene copolymer; STAPHYLOID AC-3355, STAPHYLOID AC3364, STAPHYLOID TR-2105, STAPHYLOID TR-2102, STAPHYLOID TR-2122, STAPHYLOID IM-101, STAPHYLOID IM-203, STAPHYLOID IM-301, STAPHYLOID IM-401, and STAPHYLOID IM-406, each of which consists of acrylate-methacrylate copolymer; STAPHYLOID IM-601, which consists of acrylate-acrylonitrile-styrene copolymer; and ZEFIAC F-351G (manufactured by Aica Kogyo Company, Limited) and PARALOID EXL-2314, EXL-2611, and EXL-3387 (manufactured by Dow Chemical Japan Limited), each of which consists of polymethacrylate polymer, but are not limited thereto. One of these may be used alone, and alternatively two or more thereof may be used in combination.

[0043]

The particle size of the rubber particles is preferably 0.01 to 10 μm , and particularly preferably 0.05 to 5 μm . The particle size falling within the range inhibits increase in viscosity and makes the electrically conductive resin composition superior in electroconductivity.

[0044]

The amount of the rubber particles contained is preferably 0.01 to 20 parts by mass, further preferably 0.03 to 10 parts by mass, and most preferably 0.05 to 5 parts by mass per 100 parts by mass of the component (A). The amount falling within the range makes the electrically conductive resin composition superior in electroconductivity.

[0045]

Specific examples of the rubber particles dispersed in advance in an epoxy resin include rubber particles dispersed in an epoxy resin by using a mixing/stirring apparatus such as a hyper or homogenizer, and rubber

particles synthesized by emulsion polymerization in an epoxy resin. One of these may be used alone, and alternatively two or more thereof may be used in combination. The epoxy resin to disperse rubber particles therein is regarded as the component (A).

[0046]

Examples of commercially available products of the rubber-dispersed epoxy resin include KaneAce MX-153, MX-136, MX-257, MX-127, and MX-451 (manufactured by KANEKA CORPORATION), and ACRYSET BPF-307 and BPA-328 (manufactured by NIPPON SHOKUBAI CO., LTD.). One of these may be used alone, and alternatively two or more thereof may be used in combination.

[0047]

The electrically conductive resin composition of the present invention may contain a silane coupling agent. Examples of the silane coupling agent include: a glycidyl-group-containing silane coupling agent such as 3-glycidoxypropyltriethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 3-glycidoxypropyltrimethoxysilane, and 3-glycidoxypropylmethyldiethoxysilane; a vinyl-group-containing silane coupling agent such as vinyltris(β -methoxyethoxy)silane, vinyltriethoxysilane, and vinyltrimethoxysilane; a (meth)acryl-group-containing silane coupling agent such as γ -methacryloxypropyltrimethoxysilane; an amino-group-containing silane coupling agent such as N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, and N-phenyl- γ -aminopropyltrimethoxysilane; γ -mercaptopropyltrimethoxysilane; and γ -chloropropyltrimethoxysilane; and an oligomer of any of them, and the glycidyl-group-containing silane coupling agent is preferred for superiority in adhesion. One of those may be used alone, and alternatively two or more thereof may be used in combination.

[0048]

Examples of commercially available products of silane coupling agents include, but are not limited to: KBM-1003, KBE-1003, KBM-303, KBM-403, KBE-403, KBM-502, KBE-502, KBM-503, KBE-503, KBM-5103, KBM-1403, KBM-602, KBM-603, KBM-903, and KBE-903 (manufactured by Shin-Etsu Chemical Co., Ltd.); and Z-6610, Z-6044, Z-6825, Z-6033, and Z-6062 (manufactured by Toray-Dow Corning Co., Ltd.).

[0049]

<Curing method and cured product>

A cured product given by curing the electrically conductive resin composition of the present invention is also one aspect of the present invention. The electrically conductive resin composition of the present invention is capable of curing at low temperature for use in applications in which a heat-sensitive plastic member is used.

Any curing temperature condition may be applied without limitation, and the curing temperature is preferably 25 to 100°C, more preferably 50 to 95°, and most preferably 70 to 90°C, which is a low temperature for curing by heating. The curing time is not limited, and preferably 10 to 180 minutes, more preferably 30 to 120 minutes, and most preferably 40 to 100 minutes.

[0050]

<Applications>

Being capable of curing at low temperature, the electrically conductive resin composition of the present invention can be suitably used for members with heat-sensitive plastic or the like. Specific examples include liquid-crystal image display elements, organic EL elements, solar cell elements, camera modules, flexible printed wiring boards, wearables, and battery packs. Examples of the plastic include polypropylene, polyethylene, polyurethane, ABS, phenolic resin, CFRP (carbon-fiber-reinforced plastic), GFRP (glass-fiber-reinforced plastic), 6,6-nylon, PPS, and PBT.

[0051]

The electrically conductive resin composition of the present invention is preferably used for adherends having an outermost surface made of nickel. This is because the electrically conductive resin composition of the present invention, which has the above configuration, gives a low contact resistance value even for an adherend having an outermost surface made of nickel, which forms an oxide film, and at the same time is superior in storage stability and capable of exerting much superior handleability, although the exact reason has not been elucidated. Representative examples of adherends having an outermost surface made of nickel include, but are not limited to, nickel-plated adherends such as adherends given by subjecting a member made of SPCC (cold-rolled steel sheet), stainless steel, or copper to electroplating or electroless plating (e.g., electrical wires, printed circuit (wiring) boards).

Examples

[0052]

Next, the present invention will be described in more detail with reference to examples, but the present invention is not limited only to those examples. Unless otherwise specified, tests were conducted under an environment at 25°C and 55% RH.

[0053]

<Examples 1 to 7 and Comparative Examples 1 to 5>

To prepare electrically conductive resin compositions, components shown below were provided. Hereinafter, an electrically conductive resin composition is also called a composition, simply.

[0054]

Component (A): epoxy resin

(A-1): epoxy resin having two or more epoxy groups in one molecule

- EPICLON EXA-835LV (mixture of bifunctional bisphenol A epoxy resin and bifunctional bisphenol F epoxy resin, mass ratio: 50:50, manufactured by DIC Corporation)
- Epoxy resin component of CUREDUCT L-07N (mixture of epoxy resin (bifunctional bisphenol A epoxy resin: 91% by mass), phenolic resin (phenolnovolac resin: 4% by mass), and borate compound (2,2'-(carbonylbisoxo)bis(1,3,2-dioxaborolane-4,5-dione): 5% by mass), manufactured by SHIKOKU CHEMICALS CORPORATION)

(A-2): epoxy resin having one epoxy group in one molecule

- ED-509S (p-tertiary-butylphenyl glycidyl ether, boiling point: 294°C, manufactured by ADEKA Corporation)
- CARDURA E10P (neodecanoic acid glycidyl ester, boiling point: 278°C, manufactured by HEXION INC.)

Component (B): electrically conductive particles

(B-1): crystalline electrically conductive particles

- M27 (crystalline silver particles, flake-like, surface-treated with stearic acid, average particle size: 4.5 μm, average thickness T: 80 nm, manufactured by TOKUSEN KOGYO Co., Ltd.)

(B-2): noncrystalline electrically conductive particles

- Silbest TC-770 (noncrystalline silver particles, flake-like, surface-treated with stearic acid, average particle size: 3.5 μm, manufactured by TOKURIKI HONTEN CO., LTD.)

Component (C): polyamine-based latent curing agent

(C-1): polyamine-based latent curing agent having softening point of 50 to 129°C

- Fujicure FXR-1081 (adduct-modified aliphatic polyamine-based latent curing agent, average particle size: 5 μm, softening point: 121°C, manufactured by T&K TOKA CO., LTD.)
- Fujicure 1061 (adduct-modified aliphatic polyamine-based latent curing agent, average particle size: 5 μm,

softening point: 98°C, manufactured by T&K TOKA CO., LTD.)

- Fujicure FXR-1020 (adduct-modified aliphatic polyamine-based latent curing agent, average particle size: 5 µm, softening point: 124°C, manufactured by T&K TOKA CO., LTD.)

(C-2): polyamine-based latent curing agent having softening point of 130 to 180°C

- Fujicure FXR-1030 (adduct-modified aliphatic polyamine-based latent curing agent, average particle size: 5 µm, softening point: 140°C manufactured by T&K TOKA CO., LTD.)

Component (C'): latent curing agent other than component (C)

- Fujicure FXR-1121 (imidazole-based latent curing agent, average particle size: 5 µm, softening point: 133°C, manufactured by T&K TOKA CO., LTD.)

Optional components

- Storage stabilizer component of CUREDUCT L-07N (mixture of epoxy resin (bifunctional bisphenol A epoxy resin: 91% by mass), phenolic resin (phenolnovolac resin: 4% by mass), and borate compound (2,2'-(carbonylbisoxo)bis(1,3,2-dioxaborolane-4,5-dione): 5% by mass), manufactured by SHIKOKU CHEMICALS CORPORATION)

- Plasticizer component of CUREDUCT L-07N (mixture of epoxy resin (bifunctional bisphenol A epoxy resin: 91% by mass), phenolic resin (phenolnovolac resin: 4% by mass), and borate compound (2,2'-(carbonylbisoxo)bis(1,3,2-dioxaborolane-4,5-dione): 5% by mass), manufactured by SHIKOKU CHEMICALS CORPORATION)

The production method for the compositions according to Examples 1 to 7 and Comparative Examples 1 to 5 is as follows. A component (A), a component (B), and optional components were weighed out, and stirred with a planetary mixer for 30 minutes. Subsequently, a component (C) and component (C') were weighed out and added, and the resultant was then further stirred with a planetary mixer for 30 minutes while vacuum defoaming was performed, giving an electrically conductive resin composition.

[0055]

<Electric conductivity>

Masking tape having a width of 10 mm and a thickness of 100 µm was provided with five holes of 5 mm in diameter at intervals of 10 mm along the longitudinal direction. The masking tape was attached on an electroless nickel-plated sheet of 25 mm in width × 100 mm in length × 1.6 mm in thickness, and a composition was applied onto the electroless nickel-plated sheet having the masking tape attached thereon by using a

squeegee. In applying the composition by using a squeegee, care was taken not to allow bubbles to mix in the composition. Next, the masking tape was released, and copper chips of $2\phi \times 1$ mm that had been plated with gold was placed on the composition. After that, the resultant was heated with a hot-air drying furnace at $80^{\circ}\text{C} \times 60$ minutes or 90 minutes to cure the composition, giving a test piece. After the temperature of the test piece had decreased to room temperature, adjacent gold-plated copper chips on the composition (two chips present at positions apart from each other at an interval of 10 mm) were brought into contact with needle-shaped electrodes of a dual-display multimeter to measure the resistance, and the resistance value obtained was determined as the "contact resistance value (Ω)". For stabilizing electric conductivity, the contact resistance value is preferably 3.0Ω or less, more preferably 2.5Ω or less, and particularly preferably 2.0Ω or less (lower limit: 0Ω).

[0056]

<Bond strength>

Masking tape was attached on an electroless nickel-plated sheet of 1.6 mm in thickness $\times$ 25 mm in width $\times$ 100 mm in length to give a size of 5 mm in width $\times$ 50 μm in thickness, a composition was applied with a squeegee to form a homogenous coating film, and the masking tape was then released. A ceramic chip of $2\phi \times 1$ mm was vertically dropped from 1 cm above the coating film onto the coating film to prepare a test piece ($n = 5$). The test piece was heated with a hot-air drying furnace at $80^{\circ}\text{C} \times 60$ minutes or 90 minutes to cure the composition, giving a test piece. After the temperature of the test piece had decreased to room temperature, a digital force gauge with a contactor was moved at 50 mm/min with the nickel-plated sheet fixed, and the chip was pressed with the contactor in the direction perpendicular to the long sides of the test piece to measure the "maximum strength (N)". The "bond strength (MPa)" is calculated with reference to the bonding area, and determination is made on the basis of the following evaluation criterion. For preventing the adherend from detaching, the bond strength is preferably 20 MPa or more.

[0057]

The configurations of the compositions of Examples and Comparative Examples are shown below in Table 1. Each blank in Table 1 in the following indicates the absence of the corresponding component.

[0058]

[Table 1]

			Examp le 1	Examp le 2	Examp le 3	Examp le 4	Examp le 5	Examp le 6	Examp le 7
Compon ent (A)	(A-1)	EPICLON EXA-835LV	80	80	80	80	80	80	80
		Epoxy resin component of CUREDUCT L-07N	1.82	1.82	1.82	1.82	1.82	1.82	
	(A-2)	ED-509S	20	20	20	20	20		20
		CARDURA E10P						20	
Compon ent (B)	(B-1)	M27	60	60	60	60	60	60	60
	(B-2)	Silbest TC-770	180	180	180	180	180	180	180
Compon ent (C)	(C-1)	Fujicure FXR-1081	18.75	12.5	6.25			6.25	6.25
		Fujicure 1061				6.25			
		Fujicure FXR-1020					6.25		
	(C-2)	Fujicure FXR-1030	6.25	12.5	18.75	18.75	18.75	18.75	18.75
Component (C')		Fujicure FXR-1121							
Optional component	Storage stabilizer component of CUREDUCT L-07N		0.1	0.1	0.1	0.1	0.1	0.1	
	Plasticizer component of CUREDUCT L-07N		0.08	0.08	0.08	0.08	0.08	0.08	
Total			367	367	367	367	367	367	365
Contact resistance value (80°Cx60 min)[Ω]			1.7	0.40	0.16	0.28	0.16	0.12	0.16
Contact resistance value (80°Cx90 min)[Ω]			2.2	0.38	0.18	0.26	0.17	0.11	0.18
Bond strength (80°Cx60 min)[MPa]			24.8	26.8	24.4	25.8	20.5	24.5	24.4
Bond strength (80°Cx90 min)[MPa]			28.9	25.1	24.4	25.6	21.0	25.0	24.4

			Comparat ive Example 1	Comparat ive Example 2	Comparat ive Example 3	Comparat ive Example 4	Comparat ive Example 5
Component (A)	(A-1)	EPICLON EXA-835LV	80	80	80	80	80
		Epoxy resin component of CUREDUCT L-07N	1.82	1.82	1.82	1.82	1.82
	(A-2)	ED-509S	20	20	20	20	20
		CARDURA E10P					
Component (B)	(B-1)	M27	60	60	60	60	60
	(B-2)	Silbest TC-770	180	180	180	180	180
Component (C)	(C-1)	Fujicure FXR-1081	25		6.25	6.25	
		Fujicure 1061				18.75	
		Fujicure FXR-1020					
	(C-2)	Fujicure FXR-1030		25			6.25
Component (C')		Fujicure FXR-1121			18.75		18.75
Optional component		Storage stabilizer component of CUREDUCT L-07N	0.1	0.1	0.1	0.1	0.1
		Plasticizer component of CUREDUCT L-07N	0.08	0.08	0.08	0.08	0.08
Total			367	367	367	367	367
Contact resistance value (80°Cx60 min)[Ω]			9.3	0.13	5.5	500	27.0
Contact resistance value (80°Cx90 min)[Ω]			7.0	0.12	4.0	300	5.0
Bond strength (80°Cx60 min)[MPa]			28.9	16.2	9.3	24.3	5.2
Bond strength (80°Cx90 min)[MPa]			33.8	12.0	11.2	24.5	8.5

[0059]

Examples 1 to Examples 7 were found to give cured products superior in electric conductivity and bond strength even after curing at a low temperature of 80°C. In particular, it was found from Examples 1 to 3 that a high proportion of the (C-2) in the component (C) results in a cured product superior in electric conductivity. In contrast to them, it is understood that Comparative Examples 1 and 4, which were compositions free from (C-2), gave cured products poor in electric conductivity. Comparative Example 2, which was a composition free from (C-1), gave a cured product poor in bond strength. Comparative Examples 3 and 5, which contained the component (C') in place of the (C-1) or the (C-2), were found to result in poor electric conductivity and bond strength.

Industrial Applicability

[0060]

The electrically conductive paste according to the present invention has superior electroconductivity and bond strength and thus is useful for electroconducting and bonding applications for recent downsized electric and electronic parts, and, in particular, gives lower resistance values to metals that are likely to cause deterioration in electroconductivity such as nickel. By virtue of these characteristics, the present invention can be used for assembling various electric and electronic parts, and may be widely used for various applications.

[0061]

The present application is based on Japanese Patent Application No. 2023-181725 filed on October 23, 2023, and the contents disclosed therein are entirely incorporated herein by reference.

CLAIMS

Claim 1. An electrically conductive resin composition comprising components (A) to (C), wherein the component (C) comprises (C-1) and (C-2), and

the component (A) is an epoxy resin,

the component (B) is an electrically conductive particle,

the component (C) is a polyamine-based latent curing agent,

the (C-1) is a polyamine-based latent curing agent having a softening point of 50 to 129°C, and

the (C-2) is a polyamine-based latent curing agent having a softening point of 130 to 180°C.

Claim 2. The electrically conductive resin composition according to claim 1, wherein the component (A) comprises a bisphenol epoxy resin.

Claim 3. The electrically conductive resin composition according to claim 1, wherein the component (A) comprises (A-1) that is an epoxy resin having two or more epoxy groups in one molecule, and (A-2) that is an epoxy resin having one epoxy group in one molecule.

Claim 4. The electrically conductive resin composition according to claim 1, wherein the component (B) comprises (B-1) that is a crystalline electrically conductive particle.

Claim 5. The electrically conductive resin composition according to claim 4, wherein the component (B) comprises the (B-1) that is a crystalline electrically conductive particle and (B-2) that is a noncrystalline electrically conductive particle.

Claim 6. The electrically conductive resin composition according to claim 1, wherein the component (C) is an aliphatic polyamine-based latent curing agent.

Claim 7. The electrically conductive resin composition according to claim 1, wherein the component (C) is an adduct-modified polyamine-based latent curing agent.

Claim 8. The electrically conductive resin composition according to claim 1, wherein the component (C) comprises only the (C-1) and the (C-2).

Claim 9. The electrically conductive resin composition according to claim 1, wherein a mass ratio between the (C-1) and the (C-2) is 10:90 to 90:10.

Claim 10. A cured product given by curing the electrically conductive resin composition according to claim 1.