

DESCRIPTION

TITLE OF INVENTION: CONDUCTIVE PASTE COMPOSITION

5 TECHNICAL FIELD

[0001] The present invention relates to a thermosetting conductive paste composition, and in particular to a conductive paste composition that can be suitably used in the field of electronic components.

10 BACKGROUND ART

[0002] In the related art, in the field of electronic components, a technique of using a conductive paste composition has been widely used as one of methods for forming electrical connections. Various types of such conductive paste compositions are known, and examples of a thermosetting conductive paste composition include one that contains a conductive powder
15 and an epoxy resin as resin components.

[0003] The epoxy resin has advantages such as good adhesive properties to metals that constitute electronic components, good heat resistance, and relatively small volume shrinkage when cured. For this reason, epoxy resins are widely used as resin components of conductive paste compositions.

20 [0004] In recent years, there has been an increasing demand for electronic components to be smaller, lighter, more precise, and more reliable. Therefore, various studies have been conducted on conductive paste compositions to satisfy such requirements of electronic components. For example, Patent Literature 1 discloses a conductive adhesive that uses a liquid epoxy resin and a solid epoxy resin in combination to achieve both stress relaxation and heat
25 resistance when mounting a chip component on a substrate.

CITATION LIST

PATENT LITERATURE

[0005] Patent Literature 1: JP2007-277384A

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SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] Here, a conductive paste composition containing an epoxy resin as a resin component

is required to have both thermal shock resistance and moist heat resistance after curing. However, when the resin component is an epoxy resin, attempts to improve the thermal shock resistance tend to result in a decrease in the moist heat resistance.

[0007] In recent years, as described above, higher demands have been placed on electronic components, and therefore the conductive paste composition is required to achieve both higher thermal shock resistance and higher moist heat resistance. However, no conductive paste composition containing an epoxy resin has been known that can more favorably achieve both the thermal shock resistance and the moist heat resistance. For example, the conductive adhesive described in Patent Literature 1 aims to achieve both stress relaxation and heat resistance as described above, but does not consider thermal shock resistance or moist heat resistance at all.

[0008] The present invention has been made to solve such a problem, and an object thereof is to provide a conductive paste composition containing an epoxy resin as a resin component and capable of achieving good thermal shock resistance and good moist heat resistance after curing.

SOLUTION TO PROBLEM

[0009] In order to solve the above-mentioned problem, a conductive paste composition according to the present disclosure has a configuration of including:

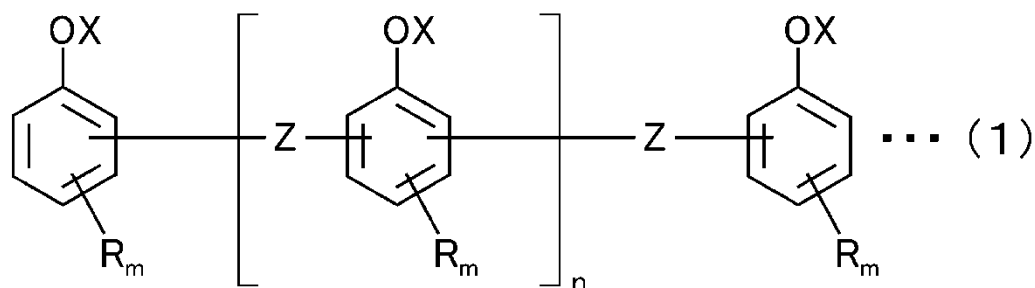
20 a (A) conductive powder; and
resin components, in which
the resin components include a (B) epoxy resin, a (C) curing agent, and a (D) curing accelerator,

25 the (B) epoxy resin contains at least one type of epoxy resin having an epoxy equivalent of 500 g/eq or more, and

the (C) curing agent is a phenolic ester compound having a structure represented by the following general formula (1).

[0010]

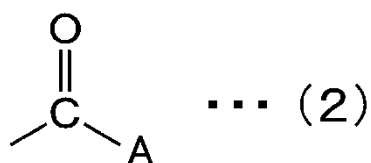
[Chem. 1]



[0011] Provided that R in the formula (1) represents an alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted phenyl group, a substituted or unsubstituted aralkyl group, an alkoxy group, or a halogen atom, X in the formula (1) represents a hydrogen atom or an ester structure represented by the following general formula (2), A in the formula (2) represents an alkyl group having 1 to 6 carbon atoms.

[0012]

[Chem. 2]



Z in the formula (1) represents a divalent hydrocarbon group having 1 to 15 carbon atoms, m in the formula (1) represents an integer of 0 to 4, n in the formula (1) represents a number of 0 to 2 on average, R, X, Z, and A in the formula (1) may represent the same substituent or atom or may represent different substituents or atoms, and m in the formula (1) may represent the same integer or may represent different integers.

[0013] According to the above configuration, the (B) epoxy resin contained as a resin component uses one or more resins having an epoxy equivalent of 500 g/eq or more, and the (C) curing agent uses a phenolic ester compound represented by the general formula (1). Accordingly, a resulting cured product of the conductive paste composition can achieve both good thermal shock resistance and good moist heat resistance while maintaining good electrical properties. Therefore, it is possible to provide a conductive paste composition containing an epoxy resin as a resin component and capable of achieving good thermal shock resistance and good moist heat resistance after curing.

[0014] In the conductive paste composition having the above configuration, the (B) epoxy resin may contain 30 mass% or more of the epoxy resin having the epoxy equivalent of 500

g/eq or more.

[0015] In the conductive paste composition having the above configuration, an esterification rate of the (C) curing agent may be 70% or more.

[0016] In the conductive paste composition having the above configuration, the (C) curing agent may be compounded in an amount within a range of 3 parts by mass to 150 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0017] In the conductive paste composition having the above configuration, the (A) conductive powder may include at least one selected from the group consisting of silver powder, copper powder, silver-coated copper powder, silver-coated nickel powder, silver-coated aluminum powder, and silver-coated glass powder.

[0018] The conductive paste composition having the above configuration may be used by being applied to a base material by a printer, a dispenser, or by dipping.

[0019] The conductive paste composition having the above configuration may be used by being applied to an electrode of an electronic component.

ADVANTAGEOUS EFFECTS OF INVENTION

[0020] According to the above configuration, the present invention has an effect of being capable of providing a conductive paste composition containing an epoxy resin as a resin component and capable of achieving good thermal shock resistance and good moist heat resistance after curing.

BRIEF DESCRIPTION OF DRAWINGS

[0021] FIG. 1 is a plan view illustrating a shape of a conductor pattern (cured product) obtained by curing a conductive paste composition according to Examples of the present disclosure, for evaluating a conductor resistance of the conductor pattern.

FIG. 2 is a model diagram schematically illustrating a configuration of an evaluation sample used to evaluate a connection resistance and adhesive strength of conductive paste compositions after curing in Examples and the like of the present disclosure.

DESCRIPTION OF EMBODIMENTS

[0022] A representative embodiment of the present disclosure will be described below. A conductive paste composition according to the present disclosure contains a (A) conductive powder and a resin component, and the resin component includes a (B) epoxy resin, a (C) curing

agent, and a (D) curing accelerator. Here, the (B) epoxy resin contains at least one epoxy resin having an epoxy equivalent of 500 g/eq or more. Furthermore, the (C) curing agent is a compound having a structure represented by a general formula (1) described below, that is, a compound obtained by esterifying a phenolic hydroxyl group of a polyhydric phenol compound.

5 Note that in the present disclosure, this compound is referred to as a phenolic ester compound.
[0023] [(A) Conductive Powder]

A specific configuration of the (A) conductive powder contained in the conductive paste composition according to the present disclosure is not particularly limited, and any conductive powder known in the field of conductive paste compositions can be suitably used.

10 Typical examples thereof include at least one selected from the group consisting of silver powder, copper powder, silver-coated copper powder, silver-coated nickel powder, silver-coated aluminum powder, and silver-coated glass powder.

[0024] In the present disclosure, in Examples described below, typical examples of the (A) conductive powder include flaky or spherical silver powder, and spherical silver-coated copper powder. Therefore, in the present disclosure, a powder containing at least silver is used as the
15 (A) conductive powder. For convenience of explanation, a powder containing silver will be referred to as a "silver-based powder" as appropriate.

[0025] Specific examples of the silver-based powder include silver powder that is essentially made of silver, a silver-coated powder in which a surface of a powder (main powder) that is
20 made of a material other than silver is coated with silver, and a silver alloy powder that is made of an alloy containing silver (silver alloy).

[0026] The silver powder is powder made only of silver, but it goes without saying that the silver powder may contain known unavoidable impurities. Even in the case of the silver alloy powder, one that has a purity that is recognized as "silver-made" according to various known
25 standards can be treated as the silver powder in the present disclosure.

[0027] A specific configuration of the silver-coated powder is not particularly limited, and the main powder made of a material other than silver may be made of a metal or a material other than metals. Examples of the material other than metals include known resin materials, known ceramic materials, and glass. If the main powder is made of a resin material, the resin
30 material needs to have such heat resistance that the powder shape (particle shape) thereof can be maintained even at a heating temperature for curing the conductive paste composition according to the present disclosure.

[0028] Examples of the silver-coated powder in which the main powder is made of a metal,

that is, a silver-coated metal powder, include, but are not limited to, silver-coated copper powder, silver-coated copper alloy powder, silver-coated nickel powder, and silver-coated aluminum powder. The silver-coated powder in which the main powder is glass, that is, a silver-coated glass powder, is not particularly limited in terms of a specific type of glass. Examples thereof include various known glass powders coated with silver.

[0029] The silver-coated powder in which the main powder is a resin, that is, a silver-coated resin powder, may be, but is not limited to, a silver-coated silicone resin powder. The silver-coated powder in which the main powder is a ceramic material, that is, a silver-coated ceramic powder, may be, but is not limited to, silver-coated alumina powder.

[0030] When the silver-based powder is a silver-coated powder, the amount of silver used for coating the surface of the main powder, that is, the amount of silver coating, is not particularly limited and can be set appropriately depending on various conditions. The amount of silver coating can be increased or decreased depending on a volume resistivity and other factors required for an application of the conductive paste composition according to the present disclosure (an application of a cured product). Alternatively, the amount of silver coating can be increased or decreased depending on the material (conductivity) of the main powder. Note that the amount of silver coating can be represented as a ratio of a mass of silver for coating to a total mass of the silver-coated powder (mass ratio, for example, percentage (mass%)).

[0031] A specific shape of the silver-based powder (or other conductive powders) is not particularly limited, and may be spherical (granular) or flaky (sheet-like or scale-like). Note that the flaky powder may be a powder that has a shape similar to a flat plate or a thin rectangular parallelepiped when viewed as a whole, even when unevenness or deformation is partially observed. The spherical powder may be a powder that has a three-dimensional shape closer to a cube than a rectangular parallelepiped when viewed as a whole, even when unevenness or deformation is partially observed.

[0032] Specific physical properties of the silver-based powder (or other conductive powders) are not particularly limited, and an average particle size, a specific surface area, a tap density, and the like thereof may be within known ranges. For example, if the silver-based powder is a flaky powder, an average particle size D50 thereof may be in a range of, for example, 0.5 μm to 20 μm , a BET specific surface area thereof may be in a range of, for example, 0.1 m^2/g to 2.0 m^2/g , a tap density thereof may be in a range of, for example, 0.5 g/cm^3 to 10 g/cm^3 , and an aspect ratio thereof may be in a range of, for example, 5 to 15. If the silver-based powder is a spherical powder, the average particle size D50 thereof may be in a range of 0.1 μm to 10 μm ,

the BET specific surface area thereof may be in a range of 0.5 m²/g to 2.0 m²/g, and the tap density thereof may be, for example, 1.0 g/cm³ to 10 g/cm³. Conductive powders other than the silver-based powder may also be used as long as physical properties thereof fall within the above ranges.

5 [0033] Note that a method for measuring (evaluating) the average particle size D50 of the conductive powder is not particularly limited, and in the present disclosure, the average particle size D50 may be measured (evaluated) by a laser diffraction method using a Microtrac particle size distribution measuring device, as in Examples described below. A method for evaluating the BET specific surface area of the conductive powder is not particularly limited, and the BET
10 specific surface area may be measured and evaluated by a BET one-point method using nitrogen adsorption using a known specific surface area meter, as in Examples described below. A method for evaluating the tap density of the conductive powder is not particularly limited, but as in Examples described below, the tap density may be evaluated by tapping a sample under predetermined conditions using a known tap density measuring device and calculating a ratio
15 of a sample mass to a sample volume after tapping.

[0034] Various conditions in the various measurement methods or evaluation methods for the (A) conductive powder containing these silver-based powders can be conditions known in the field of resin-type conductive pastes (for example, conditions described in the published patent applications by the applicant of the present application).

20 [0035] Regardless of whether the silver-based powder is a silver powder (or a silver alloy powder) or a silver-coated powder, or whether the shape of the silver-based powder is flaky or spherical, a method for producing the powder is not particularly limited, and any known method can be used.

[0036] When the silver powder (or silver alloy powder) is a flaky powder, for example, the
25 flaky powder can be produced by using a spherical powder produced by a known method as a base powder and performing a known mechanical treatment on the base powder. A particle size, a degree of aggregation, and other physical properties of the base powder can be appropriately selected depending on, for example, an intended use of the conductive paste composition (a type of an electrode, an electrical wiring, or the like, which is the cured product, or a type of an
30 electronic component, an electronic device, or the like that includes such an electrode, an electrical wiring, or the like).

[0037] When the silver powder (or silver alloy powder) is a spherical powder, the method for producing the powder is not particularly limited, and examples of the powder include a

powder produced by a wet reduction method, and spherical powders produced by other known methods such as an electrolysis method or an atomization method. In the case of the silver-coated powder, the surface of the flaky or spherical main powder produced as described above may be coated with silver by a known method.

5 [0038] In the conductive paste composition according to the present disclosure, at least a silver-based powder may be used as the (A) conductive powder, but a conductive powder other than the silver-based powder may also be used in combination. Examples of such other conductive powders include, but are not limited to, gold powder, copper powder, palladium powder, nickel powder, aluminum powder, lead powder, and carbon powder. A typical example
10 thereof is copper powder.

[0039] When a plurality of types of powders are used in combination as the (A) conductive powder, compounding ratios (compounding amounts) of these powders are not particularly limited. For example, when a silver-based powder is used in combination with a conductive powder other than the silver-based powder, the silver-based powder in the entire (A) conductive
15 powder needs to be contained at more than 10 mass%, and may be contained in an amount of 50 mass% or more, 90 mass% or more, or 95 mass% or more. When another conductive powder is used in combination, the compounding amount thereof can be appropriately determined depending on various conditions required for the resulting cured product.

[0040] [(B) Epoxy Resin]

20 A specific configuration of the (B) epoxy resin used as one of resin components in the present disclosure is not particularly limited, but at least one epoxy resin having an epoxy equivalent of 500 g/eq or more is used as the (B) epoxy resin.

[0041] For convenience of explanation, the epoxy resin having an epoxy equivalent of 500 g/eq or more will be referred to as a "first epoxy resin", and an epoxy resin having an epoxy
25 resin of less than 500 g/eq will be referred to as a "second epoxy resin". In the present disclosure, as the (B) epoxy resin, only the first epoxy resin may be used, or the first epoxy resin and the second epoxy resin may be used in combination.

[0042] When the first epoxy resin is used as the (B) epoxy resin, and a phenolic ester compound is used as the (C) curing agent, as described below, the resulting cured product of
30 the conductive paste composition can achieve both good thermal shock resistance and good moist heat resistance while maintaining good electrical properties.

[0043] When the first epoxy resin and the second epoxy resin are used in combination, a content of the first epoxy resin contained in the entire (B) epoxy resins is not particularly limited,

and typically can be 30 mass% or more. If the content of the first epoxy resin is 30 mass% or more, it is possible to more favorably achieve both the thermal shock resistance and the moist heat resistance.

[0044] In the present disclosure, as the (B) epoxy resin, only one type of first epoxy resin may be used, or two or more types thereof may be used appropriately in combination. When the second epoxy resin is used in combination as the (B) epoxy resin, only one type of the second epoxy resin may be used, or two or more types thereof may be used appropriately in combination.

[0045] In the present disclosure, regardless of whether it is the first epoxy resin or the second epoxy resin, the specific type of the epoxy resin used as the (B) epoxy resin is not particularly limited. Typical examples thereof include a polyhydric epoxy resin having two or more oxirane rings (epoxy groups) in one molecule.

[0046] Examples of such a polyhydric epoxy resin include glycidyl ether type resins, glycidyl amine type resins, glycidyl ester type resins, and alicyclic type resins. The glycidyl ether type resins can be obtained by, for example, reacting epichlorohydrin with novolak, polyhydric phenol, polyhydric alcohol, or the like. Examples of the novolak include phenol novolak and cresol novolak. Examples of the polyhydric phenol include bisphenol A, hydrogenated bisphenol A, bisphenol F, bisphenol AD, and resorcinol. Examples of the polyhydric alcohol include ethylene glycol, neopentyl glycol, glycerin, trimethylolpropane, pentaerythritol, triethylene glycol, and polypropylene glycol. Examples of monofunctional glycidyl ether type epoxy resins include phenyl glycidyl ether. The glycidyl amine type resins can be obtained by, for example, reacting epichlorohydrin with a polyamino compound such as ethylenediamine, triethylenetetramine, or aniline. The glycidyl ester type resins can be obtained by, for example, reacting epichlorohydrin with a polyvalent carboxyl compound such as adipic acid, phthalic acid, or isophthalic acid. The alicyclic type resins are synthesized by, for example, oxidation of olefins. These epoxy resins may be used alone or in combination of two or more types thereof.

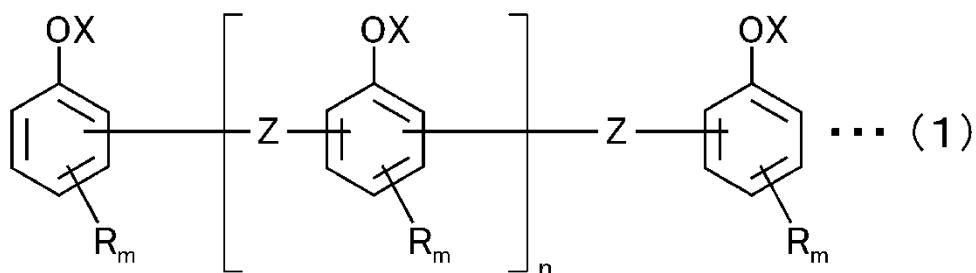
[0047] In Examples described below, a commercially available bisphenol A epoxy resin is used as the first epoxy resin (epoxy equivalent: 500 g/eq or more), and a commercially available bisphenol A epoxy resin, bisphenol F epoxy resin, or a phenol novolak type epoxy resin is used as the second epoxy resin (epoxy equivalent: less than 500 g/eq).

[0048] [(C) Curing Agent]

In the present disclosure, the (C) curing agent used as one of the resin components

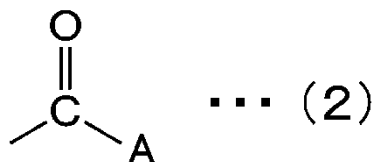
together with the (B) epoxy resin is a compound obtained by esterifying a phenolic hydroxyl group of a polyhydric phenol compound with an organic acid. More specifically, the (C) curing agent according to the present disclosure may be a phenolic ester compound having a structure represented by the following general formula (1).

5 [0049] [Chem. 3]



[0050] In the general formula (1), R represents an alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted phenyl group, a substituted or unsubstituted aralkyl group, an alkoxy group, or a halogen atom. X in the general formula (1) represents a hydrogen atom or an ester structure represented by the following general formula (2). In the general formula (2), A represents an alkyl group having 1 to 6 carbon atoms. Z in the general formula (1) represents a divalent hydrocarbon group having 1 to 15 carbon atoms.

[0051] [Chem. 4]



15 [0052] R, X, Z, and A in the general formula (1) each independently represents the aforementioned substituent or atom. That is, in the general formula (1), R, X, Z, and A may each represent the same substituent or atom, or may each represent different substituents or atoms (including a case where some of R, X, Z, and A in the molecule each represent the same substituent or atom and the others each represent different substituents or atoms).

20 [0053] In the general formula (1), m represents an integer of 0 to 4, and n in the general formula (1) represents a number of 0 to 2 on average. In the formula (1), m may all be the same integer or may be different integers (including a case where some of m in the molecule represent the same integer and the others represent different integers).

[0054] By using such a phenolic ester compound as the (C) curing agent for the (B) epoxy resin containing the first epoxy resin, the resulting cured product of the conductive paste

composition can achieve good electrical properties as well as good thermal shock resistance and good moist heat resistance.

[0055] An esterification rate of the phenolic ester compound as the (C) curing agent is not particularly limited, and is typically 70% or more, or may be 80% or more, or may be 90% or more. If the esterification rate of the phenolic ester compound is 70% or more, when the phenolic ester compound is used as the (C) curing agent for the (B) epoxy resin containing at least one type of the first epoxy resin as the (B) epoxy resin, it is possible to easily achieve good thermal shock resistance and good moist heat resistance in the cured product of the obtained conductive paste composition.

[0056] A synthesis method (production method) of the phenolic ester compound represented by the general formula (1) is not particularly limited, and known methods can be suitably used. For example, in Examples described below, a commercially available phenolic resin (for example, phenol novolak resin or cresol novolak resin) is reacted with a carboxylic acid anhydride (for example, acetic anhydride or propionic anhydride) by a known method to synthesize a phenolic ester compound. Note that the esterification rate of the phenolic ester compound used in Examples described below is 90% or more (95% or 93%).

[0057] In the present disclosure, an amount of the (C) curing agent used (a compounding amount of the (C) curing agent in the conductive paste composition) is not particularly limited. Typically, when a total amount of the (B) epoxy resin contained in the conductive paste composition is 100 parts by mass, the (C) curing agent may be compounded in an amount ranging from 3 parts by mass to 150 parts by mass. In Examples described below, the amount of the (C) curing agent used per 100 parts by mass of the (B) epoxy resin is exemplified as 4.1 parts by mass to 33.3 parts by mass.

[0058] In the present disclosure, a phenol compound before esterification used in the synthesis of the phenolic ester compound as the (C) curing agent is not particularly limited. Specific examples of the phenol compound include known polyhydric phenol compounds such as phenol novolak resin, cresol novolak resin, aromatic hydrocarbon formaldehyde resin-modified phenol resin, dicyclopentadiene phenol addition type resin, phenol aralkyl resin (ZYLOCK resin), naphthol aralkyl resin, triphenylol methane resin, tetraphenylol ethane resin, naphthol novolak resin, naphthol-phenol co-condensed novolak resin, naphthol-cresol co-condensed novolak resin, and terpene phenol resin.

[0059] An organic acid used to esterify these phenolic compounds is not particularly limited. Typical examples thereof include acetic acid, propionic acid, butyric acid, valeric acid, oxalic

acid, succinic acid, maleic acid, phthalic acid, and benzoic acid. As mentioned above, the organic acid may be an anhydride.

[0060] Note that only one type of the phenolic ester compound as the (C) curing agent may be used, or two or more types thereof may be used appropriately in combination. Known curing agents other than the phenolic ester compounds may be used in combination as long as the physical properties of the resulting conductive paste composition or the cured product thereof are not affected.

[0061] [(D) Curing Accelerator]

In the present disclosure, the (D) curing accelerator is used as a resin component together with the (B) epoxy resin and the (C) curing agent. The specific (D) curing accelerator is not particularly limited, and may be a known compound used to cure the first epoxy resin, or the first epoxy resin and the second epoxy resin used as the (B) epoxy resin.

[0062] Specific examples of the (D) curing accelerator include acid anhydrides such as phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride, methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, and succinic anhydride; imidazoles such as imidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 1-benzyl-2-methylimidazole, 2-phenyl-4-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-aminoethyl-2-methylimidazole, 1-methylimidazole, and 2-ethylimidazole; tertiary amines such as dimethyloctylamine, dimethyldecylamine, dimethylaurylamine, dimethylmyristylamine, dimethylpalmitylamine, dimethylstearylamine, dimethylbehenylamine, dilaurylmonoethylamine, methyldidecylamine, methyldioleylamine, triallylamine, triisopropanolamine, triethylamine, 3-(dibutylamino)propylamine, tri-n-octylamine, 2,4,6-trisdimethylaminomethylphenol, triethanolamine, methyldiethanolamine, and diazabicycloundecene; Lewis acids containing boron fluoride, such as boron trifluoride ethyl ether, boron trifluoride phenol, boron trifluoride piperidine, boron trifluoride acetate, boron trifluoride monoethylamine, boron trifluoride triethanolamine, and boron trifluoride monoethanolamine, or compounds thereof; amine adducts such as Amicure series PN-23 or MY-24 available from Ajinomoto Fine-Techno Co., Inc., and Fujicure series FXR-1020 or FXR-1030 available from Fuji Kasei Industries Co., Ltd.; and dicyandiamide.

[0063] Only one type of these (D) curing accelerators may be used alone or a combination of two or more types thereof may be used appropriately. An amount or conditions of use of the (D) curing accelerator are not particularly limited, and the (D) curing accelerator may be used

in a known amount or under known conditions.

[0064] In Examples described below, Examples 1 to 14 and Comparative Examples 1 to 7 all use 2-ethyl-4-methylimidazole as the (D) curing accelerator.

[0065] [Production Method and Use of Conductive Paste Composition]

5 A method for producing the conductive paste composition according to the present disclosure is not particularly limited, and known methods can be suitably used. As a typical example, the above-described components (A) to (D) and other components that are added or compounded as necessary may be compounded in predetermined compounding ratios (in terms of mass), and then made into a paste using a known kneading device. An example of the
10 kneading device is a three-roll mill.

[0066] The compounding amount (content) of each of the components (A) to (D) in the conductive paste composition according to the present disclosure is not particularly limited. When a total amount of the (A) conductive powder and the resin components is 100 mass%, the compounding amount of the (A) conductive powder needs to be in a range of 70 mass% to
15 99 mass%, may be in a range of 80 mass% to 98 mass%, or may be in a range of 85 mass% to 95 mass%.

[0067] If the compounding amount of the (A) conductive powder is less than 70 mass%, a contact density between particles of the (A) conductive powder in the cured conductive paste composition (cured product) will be small, and there is a concern that poor contact between
20 particles in the (A) conductive powder results in insufficient conductivity, which may lead to an increase in volume resistivity. On the other hand, if the content of the (A) conductive powder is more than 99 mass%, the amount of the resin components will be reduced, and there is a concern that the (A) conductive powder may not be uniformly dispersed.

[0068] Note that the conductive paste composition according to the present disclosure may
25 contain, as necessary, a solvent and various additives known in the field of conductive paste compositions, in addition to the aforementioned (A) conductive powder and the resin component ((B) epoxy resin, (C) curing agent, and (D) curing accelerator). The additives are not particularly limited, and specific examples thereof include leveling agents, antioxidants, ultraviolet absorbers, silane coupling agents, antifoaming agents, and viscosity modifiers.
30 These additives can be added within a range that does not impair the functions and effects of the present invention.

[0069] The solvent is added to adjust the physical properties, such as the viscosity or fluidity, of the conductive paste composition according to the present disclosure. The physical properties

of the conductive paste composition according to the present disclosure are not particularly limited, and the viscosity thereof can be, for example, within a range of 75 Pa·s to 100 Pa·s, from the viewpoint of convenience in forming patterns of electrodes, electrical wirings, and the like, particularly efficiency in screen printing. If the viscosity of the conductive paste composition is within this range, pattern formation by screen printing can be carried out satisfactorily.

[0070] A specific type of the solvent is not particularly limited, and examples thereof include saturated hydrocarbons such as hexane; aromatic hydrocarbons such as toluene; glycol ethers (cellosolves) such as ethyl cellosolve, butyl cellosolve, and butyl cellosolve acetate; glycol ethers such as diethylene glycol diethyl ether and butyl diglycol (butyl carbitol, diethylene glycol monobutyl ether); acetate esters of glycol ethers such as butyl diglycol acetate and butyl carbitol acetate; alcohols such as diacetone alcohol, terpineol, and benzyl alcohol; ketones such as cyclohexanone and methyl ethyl ketone; and esters such as DBE, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate. Only one type of these solvents may be used or combination of two or more types thereof may be used appropriately.

[0071] A compounding amount of the solvent is not particularly limited, and can be added in an amount that allows the viscosity or fluidity of the conductive paste composition according to the present disclosure to be adjusted within a suitable range. Note that if the content of the solvent exceeds 40 mass% with respect to the entire conductive paste composition, the fluidity suitable for printing may not be obtained, resulting in a decrease in printability, although the fluidity may also depend on the types of other components or the composition of the conductive paste composition.

[0072] A method for forming a predetermined pattern on a base material using the conductive paste composition according to the present disclosure is not particularly limited, and various known forming methods can be suitably used. Typical examples thereof include a method using a printer that adopts a screen printing method, but other printing methods such as gravure printing, offset printing, inkjet printing, dispenser printing, and dip printing (dipping) can also be applied.

[0073] A method for forming a pattern to be a cured product of the conductive paste composition according to the present disclosure is not particularly limited, and various known forming methods can be suitably used. Typical examples thereof include printing methods such as screen printing, gravure printing, offset printing, inkjet printing, dispenser printing, and

dipping. Therefore, the conductive paste composition according to the present disclosure needs to be used by being applied to a base material by a printer, a dispenser, or dipping.

[0074] A method for curing the conductive paste composition according to the present disclosure is not particularly limited, and known heating methods can be suitably used depending on the types of the (B) epoxy resin and the (C) curing agent included in the resin components. In Examples described below, when preparing an evaluation sample, the conductive paste composition was applied to a substrate and heated in a hot air dryer at 200°C for 60 minutes, but it goes without saying that the present disclosure is not limited to this heating method. In the present disclosure, methods for measuring or evaluating various physical properties of the cured product of the conductive paste composition are not particularly limited, and methods exemplified in Examples described below can be suitably used.

[0075] The conductive paste composition according to the present disclosure can be suitably used in a wide range of applications in which a conductive cured product is formed by curing with heat. A typical example thereof is formation of patterned electrodes or electrical wirings on a base material. Specifically, the conductive paste composition can be suitably used for applications such as external electrodes of chip-type electronic components; electrodes or electrical wirings of components used in radio frequency identification (RFID), electromagnetic wave shielding, vibrator bonding, membrane switches, electroluminescence, and the like; and collecting electrodes of solar cells. Especially, the conductive paste composition according to the present disclosure can be suitably used for applications in which the conductive paste composition is applied to electrodes of electronic components.

[0076] As described above, the conductive paste composition according to the present disclosure has a configuration of containing the (A) conductive powder and the resin component. The resin component includes the (B) epoxy resin, the (C) curing agent, and the (D) curing accelerator. The (B) epoxy resin contains at least one epoxy resin having an epoxy equivalent of 500 g/eq or more. The (C) curing agent is a phenolic ester compound having a structure represented by the general formula (1) described above.

[0077] According to the above configuration, the (B) epoxy resin contained as a resin component uses one or more epoxy resins having an epoxy equivalent of 500 g/eq or more, and the (C) curing agent uses a phenolic ester compound represented by the general formula (1). Accordingly, a resulting cured product of the conductive paste composition can achieve both good thermal shock resistance and good moist heat resistance while maintaining good electrical properties. Therefore, it is possible to provide a conductive paste composition containing an

epoxy resin as a resin component and capable of achieving good thermal shock resistance and good moist heat resistance after curing.

Examples

[0078] The present disclosure will be described more specifically based on Examples and Comparative Examples, but the present invention is not limited thereto. Those skilled in the art can make various changes, modifications, and alterations without departing from the scope of the present invention. Note that in the following Examples, a method for evaluating the (A) conductive powder, a method for synthesizing the phenolic ester compound as the (C) curing agent, and a method for evaluating the cured product will be shown.

[0079] [Evaluation Method for (A) Conductive Powder]

(1) Average Particle Size D50

An average particle size D50 of each (A) conductive powder shown in Table 1 was evaluated by a laser diffraction method. Into a 50 ml beaker, 0.3 g of a sample of each (A) conductive powder was weighed and dispersed by adding 30 ml of isopropyl alcohol and treating the mixture for 5 minutes in an ultrasonic cleaner (manufactured by AS ONE Corporation, product name: USM-1), and the average particle size D50 thereof was measured and evaluated using a Microtrac particle size distribution measuring device (manufactured by Nikkiso Co., Ltd., product name: Microtrac particle size distribution measuring device 9320-HRA X-100).

(2) Evaluation of BET Specific Surface Area

A BET specific surface area of each (A) conductive powder shown in Table 1 was evaluated using a surface area analyzer (manufactured by Quanta Chrome, product name: Monosorb). To the surface area analyzer, 1 g of the sample of each (A) conductive powder was supplied, and the specific surface area thereof was measured and evaluated by the BET one-point method using nitrogen adsorption. Note that in the measurement of the BET specific surface area, degassing conditions before the measurement were 60°C for 10 minutes.

(3) Evaluation of Tap Density

A tap density of each (A) conductive powder shown in Table 1 was evaluated using a tap density measuring device (manufactured by Shibayama Scientific Co., Ltd., product name: bulk specific gravity measuring device SS-DA-2) according to the following calculation formula (3). Into a 20 ml test tube, 15 g of the sample of each (A) conductive powder was weighed and placed, and tapped 1,000 times at a drop of 20 mm. A sample volume (cm³) after tapping was measured using the tap density measuring device, and the tap density was

calculated and evaluated using the following calculation formula (3).

$$\text{Tap density} = \text{sample mass} / \text{sample volume after tapping} \quad (3)$$

[0082] [Evaluation Methods for Cured Product]

(1) Evaluation of Conductor Resistance

5 A conductive paste composition according to one of Examples or Comparative Examples was used to screen-print a conductor pattern 11 illustrated in FIG. 1 onto a surface of an alumina substrate which was a base material. Note that as illustrated in FIG. 1, the conductor pattern 11 has rectangular terminals 11a and 11b at both ends, and a zigzag wiring portion 11c connecting the terminals 11a and 11b. The alumina substrate on which the conductor pattern 11 was formed was heated in a hot air dryer at 200°C for 60 minutes to cure the conductor pattern 11 (conductive paste composition). In this way, an evaluation sample for evaluating the conductor resistance was prepared.

[0083] For the evaluation sample of each Example or Comparative Example, a thickness of the cured conductor pattern 11 (cured product) was measured using a surface roughness meter (manufactured by Tokyo Seimitsu Co., Ltd., product name Surfcom 480A), and an electric resistance thereof was measured using a digital multimeter (manufactured by Advantest Corporation, product name R6551). Based on the measured thickness and electric resistance and an aspect ratio of the conductor pattern 11, a volume resistivity ($\mu\Omega\cdot\text{cm}$) of the cured product of the conductive paste composition of each Example or Comparative Example, or 15 Reference Example was calculated and evaluated.

[0084] (2) Evaluation Method for Connection Resistance

As illustrated in FIG. 2, the conductive paste composition of an Example or Comparative Example was applied to a tin (Sn)-plated substrate 21 using a dispenser to form a paste layer 22 with a diameter of 2.5 mm. Thereafter, a gold-plated rivet 23 having a circular 25 fixing surface with a diameter of 5 mm was laminated on the paste layer 22. In this case, a polyimide film having a thickness of 200 μm was used as a spacer, so that a thickness of the paste layer 22 was set to 200 μm . Next, the tin-plated substrate 21 was heated in a hot air dryer at 200°C for 60 minutes to cure the paste layer 22 to obtain a cured product layer. In this way, an evaluation sample 20 for evaluating the connection resistance was produced.

30 [0085] In the evaluation sample 20, an electric resistance between the tin-plated substrate 21 and the gold-plated rivet 23 was measured using an electric resistance meter 24 (digital multimeter, manufactured by Advantest Corporation, product name: R6551), and this measured electric resistance was taken as a connection resistance of the cured product layer. The measured

connection resistance was evaluated as "A" when being less than 0.05 Ω , and evaluated as "B" when being 0.05 Ω or more.

[0086] (3) Evaluation Method for Moist Heat Resistance

The aforementioned evaluation sample for evaluating the connection resistance was stored for 1000 hours in a thermo-hygrostat (manufactured by Espec Corporation, trade name: SH-262) set at a temperature of 85°C and a humidity of 85% RH. Connection resistances of a test piece for connection resistance evaluation before and after storage were measured in the same manner as in the above-mentioned connection resistance evaluation. A change in resistance value after storage relative to an initial resistance value before storage was evaluated as "A" when being less than 10%, evaluated as "B" when being 10% or more and less than 20%, and evaluated as "C" when being 20% or more.

[0087] (4) Evaluation Method for Thermal Shock Resistance

The aforementioned evaluation sample for evaluating the connection resistance was subjected to 1000 heat cycles of holding the sample at temperatures of -55°C and +125°C for 30 minutes each, using a thermal shock device (manufactured by Espec Corporation, product name: TSE-11-A). Connection resistances of the test piece for connection resistance evaluation before and after the heat cycles were measured in the same manner as in the above-mentioned connection resistance evaluation. A change in resistance value after storage relative to an initial resistance value before storage was evaluated as "A" when being less than 10%, evaluated as "B" when being 10% or more and less than 20%, and evaluated as "C" when being 20% or more.

[0088] [(A) Conductive Powder]

In the conductive paste compositions according to Examples and Comparative Examples, the three types of powder shown in Table 1 were used in combination as the (A) conductive powder. Note that in each Example or Comparative Example, the respective conductive powders (A) are denoted by the codes shown in Table 1.

[0089]

Table 1

Code	(A) Conductive powder	Shape	Average particle size D50 [μm]	BET specific surface area [m^2/g]	Tap density [g/cm^3]
A-01	Silver powder	Flaky	6.4	0.3	5.8
A-02	Silver powder	Spherical	0.9	1.0	3.7
A-03	Silver-coated copper powder [coating amount: 10 mass%]	Spherical	3.0	0.8	3.1

[0090] [Resin Component]

In the conductive paste compositions according to Examples and Comparative Examples, five types of (B) epoxy resins and four types of (C) curing agents shown in Table 2 were used in combination as the resin components. In order to cure these resins, the (D) curing accelerator shown in Table 2 was used. Note that in each Example or Comparative Example, the resins, curing catalysts, and initiators are denoted by the codes shown in Table 2, as are the (A) conductive powders.

[0091]

Table 2

Code	Resin component	Compound name [product name]
B-01	(B) Epoxy resin	Bisphenol A-type epoxy resin (epoxy equivalent: 3,000 g/eq) [Mitsubishi Chemical Corporation, product name: jER1009]
B-02	(B) Epoxy resin	Bisphenol A-type epoxy resin (epoxy equivalent: 8,000 g/eq) [Mitsubishi Chemical Corporation, product name: jER1256]
B-03	(B) Epoxy resin	Bisphenol A-type epoxy resin (epoxy equivalent: 190 g/eq) [Mitsubishi Chemical Corporation, product name: jER828]
B-04	(B) Epoxy resin	Bisphenol F-type epoxy resin (epoxy equivalent: 170 g/eq) [Mitsubishi Chemical Corporation, product name: jER807]
B-05	(B) Epoxy resin	Phenol novolak epoxy resin (epoxy equivalent: 190 g/eq) [manufactured by DIC Corporation, product name: EPICLON N-770]
C-01	(C) Curing agent	Acetylated phenol novolak resin (esterification rate: 95%)
C-02	(C) Curing agent	Propionated cresol novolak resin (esterification rate: 93%)
C-03	(C) Curing agent	Phenol novolak resin (hydroxyl equivalent: 104 g/eq) [manufactured by DIC Corporation, product name: PHENOLITE TD-2106]
C-04	(C) Curing agent	Cresol novolak resin (hydroxyl equivalent: 119 g/eq) [manufactured by DIC Corporation, product name: PHENOLITE KA-1165]
D-01	(D) Curing accelerator	2-Ethyl-4-methylimidazole [manufactured by Shikoku Chemicals Corporation, product name: Curezol 2E4MZ]

[0092] [Synthesis of Phenolic Ester Compound]

Among the (C) curing agents shown in Table 2, the acetylated phenol novolak resin denoted by the code C-01 and the propionated cresol novolak resin denoted by the code C-02 as phenolic ester compounds were synthesized (produced) by a method described below.

[0093] (1) Synthesis of Code C-01: Acetylated Phenol Novolak Resin

Into a 3-liter, four-neck flask equipped with a thermometer, a condenser tube, a nitrogen inlet tube, and a stirrer, 212 g of a phenol novolak resin (manufactured by DIC Corporation, product name: PHENOLITE TD-2106 (code C-03 in Table 2), hydroxyl group equivalent: 106 g/eq) was placed, and 500 g of methyl isobutyl ketone was added, followed by stirring under a nitrogen atmosphere for dissolution. Further, 210 g of acetic anhydride and 200 g of pyridine were added to the solution and dissolved. The solution was then reacted at 50°C for 4 hours. Subsequently, the resulting reaction solution was diluted with 500 g of methyl isobutyl ketone and cooled. Thereafter, the cooled diluted reaction solution was thoroughly

washed with distilled water and concentrated under reduced pressure to obtain the acetylated phenol novolak resin (esterification rate 95%) denoted by the code C-01.

[0094] (2) Synthesis of Code C-02: Propionated Cresol Novolak Resin

Into a 3-liter, four-neck flask equipped with a thermometer, a condenser tube, a nitrogen inlet tube, and a stirrer, 238 g of a cresol novolak resin (manufactured by DIC Corporation, product name: PHENOLITE KA-1165 (code C-04 in Table 2), hydroxyl group equivalent: 119 g/eq) was placed, and 500 g of methyl isobutyl ketone was added, followed by stirring under a nitrogen atmosphere for dissolution. Further, 267 g of propionic anhydride and 200 g of pyridine were added to the solution and dissolved. The solution was then reacted at 50°C for 4 hours. Subsequently, the resulting reaction solution was diluted with 500 g of methyl isobutyl ketone and cooled. Thereafter, the cooled diluted reaction solution was thoroughly washed with distilled water and concentrated under reduced pressure to obtain the propionated cresol novolak resin (esterification rate 93%) denoted by the code C-02.

[0095] (Example 1)

As the (A) conductive powder, flaky silver powder denoted by the code A-01 and spherical silver powder denoted by the code A-02 in Table 1 were selected.

In the resin components, two types of epoxy resins of the first epoxy resin having an epoxy equivalent of 500 g/eq or more and the second epoxy resin having an epoxy equivalent of less than 500 g/eq were used as the (B) epoxy resin. As the first epoxy resin, the epoxy resin denoted by the code B-01 in Table 2 (epoxy equivalent: 3,000 g/eq) was selected, and as the second epoxy resin, the epoxy resin denoted by the code B-03 (epoxy equivalent: 190 g/eq) was selected.

In the resin components, a phenolic ester compound (acetylated phenol novolak resin) denoted by the code C-01 in Table 2 was selected as the (C) curing agent, and an imidazole denoted by the code D-01 in Table 2 was used as the (D) curing accelerator.

These components (A) to (D) were compounded in the composition (compounding ratios) shown in Table 3. Note that in Table 3 (and Tables 4 and 5 described below), the compounding ratios of the two types of (A) conductive powders totals 100 mass%. In Example 1, a mass ratio (A-01/A-02) of the flaky silver powder denoted by the code A-01 to the spherical silver powder denoted by the code A-02 was 50/50.

In Table 3 (and Tables 4 and 5 described below), the composition of the resin components is such that the compounding ratios of the (B) epoxy resin and the (C) curing agent totals 100 mass%. In Example 1, a mass ratio (B-01/B-03/C-01) of the first epoxy resin denoted

by the code B-01 to the second epoxy resin denoted by the code B-03 to the curing agent denoted by the code C-01 was 25/50/25.

[0100] Note that a content of the first epoxy resin in the (B) epoxy resin was 33.3 mass% ($25/(25 + 75)$), and an amount of the (C) curing agent used was 33.3 parts by mass per 100 parts by mass of the (B) epoxy resin. In Table 3 (and Tables 4 and 5 described below), a compounding amount of the (D) curing accelerator is 1 part by mass per 100 parts by mass of the resin components in total.

[0101] Furthermore, in Table 3 (and Tables 4 and 5 described below), the compounding ratios of the (A) conductive powder and the resin components are shown as mass ratios. In Example 1, a mass ratio of a total amount of the (A) conductive powder to the total amount of the (B) epoxy resin and the (C) curing agent, which are the resin components (solid content mass ratio (A)/(B) + (C)) was 93/7. The same applies to the following Examples and Comparative Examples.

[0102] The (A) to (D) components compounded according to the composition shown in Table 3 were kneaded in a three-roll mill to prepare (produce) the conductive paste composition according to Example 1.

[0103] Using the obtained conductive paste composition according to Example 1, an evaluation sample for evaluating the conductor resistance and an evaluation sample for evaluating the connection resistance (and moist heat resistance and thermal shock resistance) were prepared (produced) as described above. Using these evaluation samples, the properties (conductor resistance, connection resistance, moist heat resistance, and thermal shock resistance) of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 3.

[0104] (Examples 2 and 3)

The conductive paste composition according to Example 2 or Example 3 was prepared (produced) in the same manner as Example 1, except that the phenolic ester compound (propionated cresol novolak resin) denoted by the code C-02 in Table 2 was selected as the (C) curing agent (Example 2), or the epoxy resin denoted by the code B-02 in Table 2 (epoxy equivalent: 8,000 g/eq) was selected as the first epoxy resin and the epoxy resin denoted by the code B-04 in Table 2 (epoxy equivalent: 170 g/eq) was selected as the second epoxy resin (Example 3) in the (B) epoxy resin.

[0105] Using the obtained conductive paste compositions according to Examples 2 and 3, evaluation samples were prepared (produced) as described above. Using these evaluation

samples, the properties of the cured products of the conductive paste compositions were evaluated by the evaluation methods described above. Results are shown in Table 3.

[0106] (Examples 4 to 6)

The conductive paste compositions according to Examples 4 to 6 were prepared (produced) in the same manner as in Example 3, except that the compounding ratio of the (A) conductive powder was A-01/A-02 = 30/70 (Example 4), or, the epoxy resin denoted by the code B-03 was selected as the second epoxy resin in the (B) epoxy resin, and the solid content mass ratio was (A)/(B) + (C) = 90/10 (Example 5), or, the epoxy resin denoted by the code B-03 was selected as the second epoxy resin, and the phenolic ester compound denoted by the code C-02 was selected as the (C) curing agent (Example 6).

[0107] Using the obtained conductive paste compositions according to Examples 4 to 6, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured products of the conductive paste compositions were evaluated by the evaluation methods described above. Results are shown in Table 3.

[0108] (Example 7)

The conductive paste composition according to Example 7 was prepared (produced) in the same manner as in Example 1, except that the epoxy resin denoted by the code B-05 shown in Table 2 (epoxy equivalent: 190 g/eq) was selected as the second epoxy resin in the (B) epoxy resin and the solid content mass ratio was (A)/(B) + (C) = 95/5.

[0109] Using the obtained conductive paste composition according to Example 7, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 3.

[0110]

Component		Examples						
		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
(A) Conductive powder	Code	A-01	A-01	A-01	A-01	A-01	A-01	A-01
	Mass ratio	50	50	50	30	50	60	50
	Code	A-02	A-02	A-02	A-02	A-02	A-02	A-02
	Mass ratio	50	50	50	70	50	40	50
(B) Epoxy resin	Code	B-01	B-01	B-02	B-02	B-02	B-02	B-01
	Mass ratio	25	25	25	25	25	25	25
	Code	B-03	B-03	B-04	B-04	B-03	B-03	B-05
	Mass ratio	50	50	50	50	50	50	50
(C) Curing agent	Code	C-01	C-02	C-01	C-01	C-01	C-02	C-01
	Mass ratio	25	25	25	25	25	25	25
(D) Curing accelerator	Code	D-01	D-01	D-01	D-01	D-01	D-01	D-01
	Mass ratio	1	1	1	1	1	1	1
(A)/(B) + (C)	Mass ratio	93/7	93/7	93/7	93/7	90/10	93/7	95/5
Conductor resistance [$\mu\Omega \cdot \text{cm}$]		13	14	15	18	28	15	13
Connection resistance		A	A	A	A	A	A	A
Moist heat resistance		A	A	A	A	B	A	A
Thermal shock resistance		B	B	A	A	A	A	B

[0111] (Examples 8 to 10)

The conductive paste compositions according to Examples 8 to 10 were prepared (produced) in the same manner as in Example 3 except that the epoxy resin denoted by the code B-05 was selected as the second epoxy resin in (B) epoxy resin, and the mass ratio of the first epoxy resin to the second epoxy resin to the (C) curing agent (B-02/B-05/C-01) was 30/50/20 (Example 8), or, the epoxy resin denoted by the code B-03 was selected as the second epoxy resin, and the mass ratio of the first epoxy resin to the second epoxy resin to the (C) curing agent (B-02/B-03/C-01) was 25/55/20, and further, the solid content mass ratio was (A)/(B) + (C) = 85/15 (Example 9), or, as the (A) conductive powder, in addition to the flaky silver powder denoted by the code A-01 and the spherical silver powder denoted by the code A-02, the silver-coated copper powder denoted by the code A-03 shown in Table 1 (silver coating amount relative to copper powder: 10 mass%) was used, and the mass ratio (compounding ratio) of these (A) conductive powders was A-01/A-02/A-03 = 30/30/40 (Example 10).

[0112] Note that in Example 8, the content of the first epoxy resin in the (B) epoxy resin was 37.5 mass% ($30/(30 + 50)$), and the amount of the (C) curing agent used was 25 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0113] Using the obtained conductive paste composition according to Example 8, evaluation

samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 4.

[0114] (Example 9)

5 The conductive paste composition according to Example 9 was prepared (produced) in the same manner as in Example 4, except that the epoxy resin denoted by the code B-03 was selected as the second epoxy resin, and the mass ratio of the first epoxy resin to the second epoxy resin to the (C) curing agent (B-02/B-03/C-01) was 25/55/20, and further, the solid content mass ratio was $(A)/(B) + (C) = 85/15$. Note that in Example 9, the amount of the (C) curing agent used was 26.6 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0115] Using the obtained conductive paste composition according to Example 9, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 4.

15 [0116] (Example 10)

 The conductive paste compositions according to Examples 8 to 10 were prepared (produced) in the same manner as in Example 3 except that as the (A) conductive powder, in addition to the flaky silver powder denoted by the code A-01 and the spherical silver powder denoted by the code A-02, the silver-coated copper powder denoted by the code A-03 shown in
20 Table 1 (silver coating amount relative to copper powder: 10 mass%) was used, and the mass ratio (compounding ratio) of these (A) conductive powders was $A-01/A-02/A-03 = 30/30/40$ (Example 10).

[0117] Using the obtained conductive paste composition according to Example 10, evaluation samples were prepared (produced) as described above. Using these evaluation
25 samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 4.

[0118] (Example 11)

 The conductive paste composition according to Example 11 was prepared (produced) in the same manner as in Example 1, except that only the epoxy resin denoted by the code B-01, which is the first epoxy resin, was used as the (B) epoxy resin, and the mass ratio of the first epoxy resin to the (C) curing agent was $B-01/C-01 = 95/5$. Note that in Example 11, the content of the first epoxy resin in the (B) epoxy resin was 100 mass%, and the amount of the (C) curing agent used was 5.2 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0119] Using the obtained conductive paste composition according to Example 11, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 4.

5 [0120] (Example 12)

The conductive paste composition according to Example 12 was prepared (produced) in the same manner as in Example 11, except that, as the (B) epoxy resin, the epoxy resin denoted by the code B-01 and the epoxy resin denoted by the code B-02 were used in combination in a mass ratio of $B-01/B-02 = 50/45$. Note that in Example 12, the content of the
10 first epoxy resin in the (B) epoxy resin was 52.6 mass% ($50/(50 + 45)$), and the amount of the (C) curing agent used was 5.2 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0121] Using the obtained conductive paste composition according to Example 12, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated
15 by the evaluation methods described above. Results are shown in Table 4.

[0122] (Examples 13 and 14)

The conductive paste composition according to Example 13 or Example 14 was prepared (produced) in the same manner as in Example 11 except that the compounding ratio of the (A) conductive powder was $A-01/A-02 = 70/30$, and the mass ratio of the first epoxy
20 resin was $B-01/B-02 = 48/48$, and further, the solid content mass ratio was $(A)/(B) + (C) = 87/13$ (Example 13), or, the compounding ratio of the (A) conductive powder was $A-01/A-02 = 20/80$, and the mass ratio of the first epoxy resin was $B-01/B-02 = 70/25$, and further, the solid content mass ratio was $(A)/(B) + (C) = 91/9$ (Example 14).

[0123] Note that in Example 13, the content of the first epoxy resin in the (B) epoxy resin
25 was 50 mass% ($48/(48 + 48)$), and the amount of the (C) curing agent used was 4.1 parts by mass per 100 parts by mass of the (B) epoxy resin. In Example 14, the content of the first epoxy resin in the (B) epoxy resin was 73.6 mass% ($70/(70 + 25)$), and the amount of the (C) curing agent used was 5.2 parts by mass per 100 parts by mass of the (B) epoxy resin.

[0124] Using the obtained conductive paste compositions according to Examples 13 and 14,
30 evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured products of the conductive paste compositions were evaluated by the evaluation methods described above. Results are shown in Table 4.

[0125]

Table 4

Component		Examples						
		Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
(A) Conductive powder	Code	A-01	A-01	A-01	A-01	A-01	A-01	A-01
	Mass ratio	50	30	30	50	50	70	20
	Code	A-02	A-02	A-02	A-02	A-02	A-02	A-02
	Mass ratio	50	70	30	50	50	30	80
	Code	-	-	A-03	-	-	-	-
	Mass ratio	-	-	40	-	-	-	-
(B) Epoxy resin	Code	B-02	B-02	B-02	B-01	B-01	B-01	B-01
	Mass ratio	30	25	25	95	50	48	70
	Code	B-05	B-03	B-04	-	B-02	B-02	B-02
	Mass ratio	50	55	50	-	45	48	25
(C) Curing agent	Code	C-01	C-01	C-01	C-01	C-01	C-01	C-01
	Mass ratio	20	20	25	5	5	4	5
(D) Curing accelerator	Code	D-01	D-01	D-01	D-01	D-01	D-01	D-01
	Mass ratio	1	1	1	1	1	1	1
(A)/ (B) + (C)	Mass ratio	93/7	85/15	93/7	93/7	93/7	87/13	91/9
Conductor resistance [$\mu\Omega \cdot \text{cm}$]		18	90	20	30	45	70	90
Connection resistance		A	A	A	A	A	A	A
Moist heat resistance		A	B	B	B	B	B	B
Thermal shock resistance		A	A	B	A	A	A	A

[0126] (Comparative Examples 1 and 2)

The conductive paste composition according to Comparative Example 1 or Comparative Example 2 were prepared (produced) in the same manner as in Example 1, except that the phenol novolak resin (hydroxyl group equivalent: 104 g/eq, Comparative Example 1) denoted by the code C-03 shown in Table 2 or the cresol novolak resin (hydroxyl group equivalent: 119 g/eq, Comparative Example 2) denoted by the code C-04 shown in Table 2 was selected as the (C) curing agent instead of using the phenolic ester compound.

[0127] Using the obtained conductive paste compositions according to Comparative Examples 1 and 2, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured products of the conductive paste compositions were evaluated by the evaluation methods described above. Results are shown in Table 5.

[0128] (Comparative Example 3)

The conductive paste composition according to Comparative Example 3 was prepared (produced) in the same manner as in Example 5, except that a phenol novolak resin denoted by the code C-03 was selected as the (C) curing agent instead of using the phenolic ester compound.

5 [0129] Using the obtained conductive paste composition according to Comparative Example 3, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 5.

[0130] (Comparative Example 4)

10 The conductive paste composition according to Comparative Example 4 was prepared (produced) in the same manner as in Example 1, except that, as the (B) epoxy resin, only the second epoxy resin denoted by the code B-03 was selected instead of using the first epoxy resin having an epoxy equivalent of 500 g/eq or more, and, as the (C) curing agent, the acetylated phenol novolak resin denoted by the code C-01, which is a phenolic ester compound,
15 was used, and the mass ratio of the second epoxy resin to the (C) curing agent was B-03/C-01 = 65/35.

[0131] Using the obtained conductive paste composition according to Comparative Example 4, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated
20 by the evaluation methods described above. Results are shown in Table 5.

[0132] (Comparative Examples 5 and 6)

The conductive paste composition according to Comparative Example 5 or Comparative Example 6 was prepared (produced) in the same manner as Comparative Example 4, except that the epoxy resin denoted by the code B-05 was selected as the second epoxy resin,
25 and the propionated cresol novolak resin denoted by the code C-02, which is a phenolic ester compound, was used as the (C) curing agent (Comparative Example 5), or, the epoxy resin denoted by the code B-05 was selected, and the phenol novolak resin denoted by the code C-03, which is not a phenolic ester compound, was used as the (C) curing agent (Comparative Example 6).

30 [0133] Using the obtained conductive paste compositions according to Comparative Examples 5 and 6, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured products of the conductive paste compositions were evaluated by the evaluation methods described above. Results are shown in

Table 5.

[0134] (Comparative Example 7)

The conductive paste composition according to Comparative Example 7 was prepared (produced) in the same manner as in Example 11, except that the phenol novolak resin denoted by the code C-03, which is not a phenolic ester compound, was selected as the (C) curing agent.

[0135] Using the obtained conductive paste composition according to Comparative Example 7, evaluation samples were prepared (produced) as described above. Using these evaluation samples, the properties of the cured product of the conductive paste composition were evaluated by the evaluation methods described above. Results are shown in Table 5.

[0136]

Table 5

Component		Comparative Examples						
		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7
(A) Conductive powder	Code	A-01	A-01	A-01	A-01	A-01	A-01	A-01
	Mass ratio	50	50	50	50	50	50	50
	Code	A-02	A-02	A-02	A-02	A-02	A-02	A-02
	Mass ratio	50	50	50	50	50	50	50
(B) Epoxy resin	Code	B-01	B-01	B-02	-	-	-	B-01
	Mass ratio	25	25	25	-	-	-	95
	Code	B-03	B-03	B-03	B-03	B-05	B-05	-
	Mass ratio	50	50	50	65	65	65	-
(C) Curing agent	Code	C-03	C-04	C-03	C-01	C-02	C-03	C-05
	Mass ratio	25	25	25	35	35	35	5
(D) Curing accelerator	Code	D-01	D-01	D-01	D-01	D-01	D-01	D-01
	Mass ratio	1	1	1	1	1	1	1
(A)/ (B) + (C)	Mass ratio	93/7	93/7	93/7	93/7	93/7	93/7	93/7
Conductor resistance [$\mu\Omega \cdot \text{cm}$]		12	12	15	10	12	12	30
Connection resistance		A	A	A	A	A	A	A
Moist heat resistance		B	B	B	C	C	B	C
Thermal shock resistance		C	C	C	B	B	C	B

[0137] (Comparison between Examples and Comparative Examples)

As is clear from the results of Examples 1 to 14, by containing the first epoxy resin having an epoxy equivalent of 500 g/eq or more as the (B) epoxy resin and using a phenolic ester compound represented by the general formula (1) as the (C) curing agent, the obtained

cured product can achieve good electrical properties (conductor resistance and connection resistance) and can also achieve both good moist heat resistance and good thermal shock resistance.

[0138] As is clear from the results of Examples 1 to 10, by using, as the (B) epoxy resin, the second epoxy resin having an epoxy equivalent of less than 500 g/eq in addition to the first epoxy resin, it is possible to achieve all of good electrical properties, good moist heat resistance, and good thermal shock resistance. Alternatively, as is clear from the results of Examples 11 to 14, even when only the first epoxy resin is used as the (B) epoxy resin, it is possible to achieve all of good electrical properties, good moist heat resistance, and good thermal shock resistance.

[0139] In contrast, as is clear from the results of Comparative Examples 1 to 3, when the phenolic ester compound represented by the general formula (1) is not used as the (C) curing agent, good thermal shock resistance cannot be achieved. As is clear from the results of Comparative Examples 4 and 5, even when a phenolic ester compound having a structure represented by the general formula (1) is used as the (C) curing agent, good moist heat resistance cannot be achieved unless the first epoxy resin having an epoxy equivalent of 500 g/eq or more is used.

[0140] Furthermore, as is clear from the results of Comparative Example 6, when the phenolic ester compound represented by the general formula (1) is not used as the (C) curing agent and the first epoxy resin is not used, good thermal shock resistance cannot be achieved.

As is clear from the results of Comparative Example 7, even when only the first epoxy resin is used, good moist heat resistance cannot be achieved unless the phenolic ester compound represented by the general formula (1) is used as the (C) curing agent.

[0141] Based on the results of Comparative Examples 1 to 7, it can be seen that when the first epoxy resin is not used as the (B) epoxy resin or the phenolic ester compound represented by the general formula (1) is not used as the (C) curing agent, good electrical properties can be achieved, but either good moist heat resistance or good thermal shock resistance cannot be achieved.

[0142] Note that the present invention is not limited to the description of the above-described embodiments, and various modifications are possible within the scope of the claims.

Embodiments obtained by appropriately combining the technical means disclosed in different embodiments or a plurality of modifications are also included in the technical scope of the present invention.

INDUSTRIAL APPLICABILITY

[0143] The present invention can be suitably used in a wide range of fields, including the field of electrical equipment and electronic equipment, in which a cured product having electric conductivity is formed. Typically, the present invention can be suitably used in a wide range of fields, for example, in which a conductive layer is formed on an electrode of an electronic component by coating with a printer, a dispenser, or by dipping.

REFERENCE SIGNS LIST

[0144] 11: conductor pattern
10 11a, 11b: terminal
11c: wiring portion
20: evaluation sample
21: tin-plated substrate
22: paste layer (or cured product layer)
15 23: gold-plated rivet
24: electric resistance meter

CLAIMS

[Claim 1]

A conductive paste composition comprising:

a (A) conductive powder; and

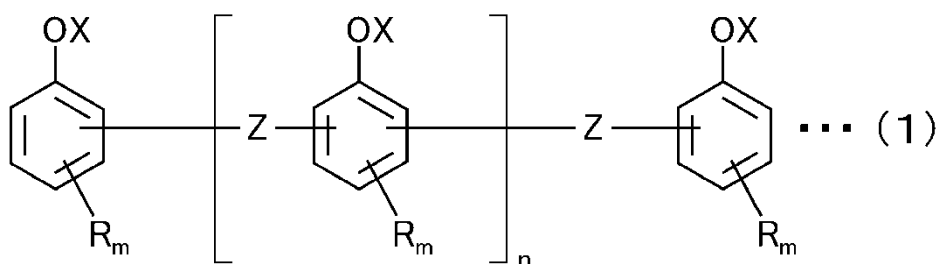
resin components, wherein

the resin components include a (B) epoxy resin, a (C) curing agent, and a (D) curing accelerator,

the (B) epoxy resin contains at least one type of epoxy resin having an epoxy equivalent of 500 g/eq or more, and

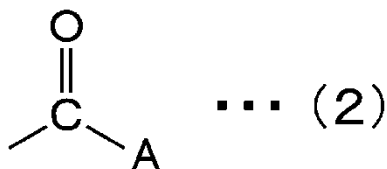
the (C) curing agent is a phenolic ester compound having a structure represented by the following general formula (1),

[Chem. 1]



provided that R in the formula (1) represents an alkyl group having 1 to 10 carbon atoms, a substituted or unsubstituted phenyl group, a substituted or unsubstituted aralkyl group, an alkoxy group, or a halogen atom, X in the formula (1) represents a hydrogen atom or an ester structure represented by the following general formula (2), A in the formula (2) represents an alkyl group having 1 to 6 carbon atoms,

[Chem. 2]



Z in the formula (1) represents a divalent hydrocarbon group having 1 to 15 carbon atoms, m in the formula (1) represents an integer of 0 to 4, n in the formula (1) represents a number of 0 to 2 on average, R, X, Z, and A in the formula (1) may represent the same substituent or atom or may represent different substituents or atoms, and m in the formula (1)

may represent the same integer or may represent different integers.

[Claim 2]

The conductive paste composition according to claim 1, wherein

5 the (B) epoxy resin contains 30 mass% or more of the epoxy resin having the epoxy equivalent of 500 g/eq or more.

[Claim 3]

The conductive paste composition according to claim 1, wherein

10 an esterification rate of the (C) curing agent is 70% or more.

[Claim 4]

The conductive paste composition according to claim 1, wherein

15 the (C) curing agent is compounded in an amount within a range of 3 parts by mass to 150 parts by mass per 100 parts by mass of the (B) epoxy resin.

[Claim 5]

The conductive paste composition according to claim 1, wherein

20 the (A) conductive powder includes at least one selected from the group consisting of silver powder, copper powder, silver-coated copper powder, silver-coated nickel powder, silver-coated aluminum powder, and silver-coated glass powder.

[Claim 6]

The conductive paste composition according to any one of claims 1 to 5, which is

25 used by being applied to a base material by a printer, a dispenser, or by dipping.

[Claim 7]

The conductive paste composition according to any one of claims 1 to 5, which is used by being applied to an electrode of an electronic component.