

DESCRIPTION

Title of Invention: Heat-Curable Conductive Paste Composition

Technical Field

[0001] The present invention relates to a heat-curable conductive paste composition. In particular, the present invention relates to a heat-curable conductive paste composition capable of forming a coating film with excellent adhesion and conductivity by being applied to or printed on a base material such as films, substrates, and electronic components, followed by heat curing.

Background Art

[0002] Conventionally, a method using a heat-curable conductive paste has been widely known as a method of forming an electrode, an electrical wire (wire), or the like on a base material such as films, substrates, and electronic components. In this method, in the case of forming a conductor pattern at a relatively low temperature, a heat-curable conductive paste containing a conductive metal powder (conductive powder) and a heat-curable resin is used. Then, the heat-curable conductive paste composition in a predetermined conductor pattern is applied to or printed on a base material and is thereafter heated so that the conductor pattern on the base material is cured by drying, whereby an electrode, a wire, or the like of a predetermined conductor pattern is formed on the base material.

[0003] In the heat-curable conductive paste compositions, an epoxy resin, a blocked polyisocyanate compound, or the like is used as the heat-curable resin, and silver is mainly used as the conductive powder.

[0004] For example, PTL 1 discloses a heat-curable conductive paste composition containing a silver powder, a blocked polyisocyanate compound, an epoxy resin, and a curing agent.

[0005] On the other hand, since silver is expensive, a heat-curable conductive paste containing, as a conductive powder, for example, copper, a copper alloy, or silver-coated copper or a silver-coated copper alloy that is copper or a copper alloy coated with silver, all of which are cheaper than silver, has been developed. PTLs 2 and 3 disclose a conductive paint formed by a method wherein a silver powder and a copper powder are together forcibly bonded together by a mechanical means to produce a silver-copper composite powder which is equivalent to the silver powder and is inexpensive, and the composite

powder is dispersed in a synthetic resin and/or a solvent.

Citation List

Patent Literatures

[0006] PTL 1: JP 2002-161123A

PTL 2: JP 56-155259A

PTL 3: JP 60-017392B

Summary of Invention

Technical Problem

[0007] As a heat-curable conductive paste containing the silver-copper composite powder disclosed in PTLs 2 and 3 instead of the silver powder in the heat-curable conductive paste composition disclosed in PTL 1, the present inventors have studied the development of a heat-curable conductive paste containing a heat-curable resin such as a blocked polyisocyanate compound, or a blocked polyisocyanate compound and an epoxy resin and containing, as a conductive powder, copper, a copper alloy, silver-coated copper that is copper coated with silver, or a coated copper alloy that is a copper alloy coated with silver.

[0008] However, compared with the case of using silver alone as the conductive powder, there is a problem in the prior art that the viscosity is increased over time during storage of the heat-curable conductive paste, resulting in decrease of the conductivity.

[0009] The present invention has been made to solve such problems. Thus, an object of the present invention is to provide a heat-curable conductive paste composition that prevents an increase in viscosity and a decrease in conductivity due to storage and having superior storage stability.

Solution to Problem

[0010] In order to solve the above problems, the heat-curable conductive paste composition according to the present invention has such a constitution that it contains (A) a conductive powder, (B) a heat-curable resin, (C) a curing agent, and (D) an inorganic ion exchanger, at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy

is used as the conductive powder (A), and a blocked polyisocyanate compound, or a blocked polyisocyanate compound and an epoxy resin are contained as the heat-curable resin (B).

[0011] In the above constitution, the inorganic ion exchanger (D) may contain any one of zirconium, magnesium, aluminum, silicon, antimony, and bismuth as a main component.

[0012] Further, in the above constitution, the content of the inorganic ion exchanger (D) may be 0.01 to 3% by mass relative to the conductive powder (A).

[0013] Moreover, in the above constitution, at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy, and silver may be used as the conductive powder (A), and the blending ratio by mass of the at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy to silver may be 100 : 0 to 1 : 99 (excluding 100 : 0).

[0014] Moreover, in the above constitution, at least one member selected from the group consisting of gold, palladium, nickel, aluminum, lead, and carbon may be further contained as the conductive powder (A).

Advantageous Effects of Invention

[0015] Owing to the above constitution, the present invention provides an effect of providing a heat-curable conductive paste composition having superior storage stability by preventing an increase in viscosity or a decrease in conductivity due to storage, even if copper, a copper alloy, silver-coated copper, or a silver-coated copper alloy is used as a conductive powder.

Brief Description of Drawings

[0016] Fig. 1 is a plan view showing a shape of a conductor pattern for evaluating characteristics (conductor resistance) of heat-curable conductive paste compositions according to the present invention.

Description of Embodiment

[0017] Hereinafter, an example of a preferred embodiment of the present invention will be specifically described.

[0018] [(A) Conductive Powder]

The conductive powder (A) in the heat-curable conductive paste composition according to the present invention contains at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy. Specific species of these materials and the blending ratio among them are not particularly limited, and the present invention achieves superior storage stability of the heat-curable conductive paste composition by preventing an increase in viscosity and a decrease in conductivity due to storage.

[0019] In the present invention, the copper alloy is an alloy that contains copper as a main component and also contains various elements (e.g. silver, zinc, nickel, cobalt, tin, lead, aluminum, chromium, cadmium, beryllium, and tellurium), and the silver-coated copper or the silver-coated copper alloy is particles in which the particle surface of copper or the copper alloy is coated with silver by a reduction plating coating method, a displacement plating coating method, or the like.

[0020] Further, “a copper alloy containing copper as a main component” means an alloy containing copper in an amount of 50% by mass or more.

[0021] As the conductive powder (A), silver may be contained in addition to at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy.

[0022] In this case, the blending ratio by mass of at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy to silver is adjusted within the range of 100 : 0 to 1 : 99 (excluding 100 : 0).

[0023] In addition, the conductive powder (A) may further contain at least one member selected from the group consisting of gold, palladium, nickel, aluminum, lead, and carbon.

[0024] In the present invention, it is preferable to define the upper limit of an alkali metal ion content in the conductive powder (A). Specifically, the sodium ion content and the potassium ion content in the conductive powder (A) are both preferably less than 200 ppm, more preferably less than 100 ppm, still more preferably less than 10 ppm. In the present invention, it is preferable that at least the sodium ion content is less than 200 ppm. If these ion contents exceed 200 ppm, a problem is likely to occur in the electrical characteristics and reliability of an electronic component or an electronic device whose

electrodes or wires are formed from the heat-curable conductive paste. On the other hand, the lower the lower limit of these ions is, the better it is.

[0025] The conductive powder (A) in the heat-curable conductive paste composition according to the present invention contains at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy. The shape of the conductive powder (A) used can be a flake-shape or a spherical shape.

[0026] The flake-shaped powder of the present invention may be a powder in the shape of a flat plate or a nearly rectangular parallelepiped having a small thickness when viewed as a whole even if partial unevenness and deformation are seen. Here, the flake shape can also be referred to as a flaky shape or a scaly shape. Further, the spherical powder of the present invention may be a powder in a three-dimensional shape that is similar to a cube rather than a rectangular parallelepiped when viewed as a whole, even if partial unevenness and deformation are seen. It is to be noted that the spherical shape may be paraphrased as a granular shape.

[0027] A preferred constitution of the flake-shaped powder among the species of the conductive powder in the present invention is specifically described. The flake-shaped powder preferably has an average particle size D50 in the range of 2 to 20 μm , a BET specific surface area in the range of 0.1 to 1 m^2/g , a tap density in the range of 3 to 7 g/cm^3 , and an aspect ratio in the range of 5 to 15.

[0028] More specifically, the average particle size D50 of the flake-shaped powder is preferably within the range of 2 to 20 μm as mentioned above, but it is more preferably within the range of 2 to 12 μm and still more preferably within the range of 6 to 10 μm . If the average particle size D50 of the flake-shaped powder is less than 2 μm , there is a tendency that the contact resistance among particles of the conductive powder is increased, and sufficient conductivity may not be obtained. On the other hand, if the average particle size D50 is larger than 20 μm , the contact resistance among particles of the conductive powder becomes smaller, but when a conductor pattern is printed using a mesh screen, the mesh screen may be clogged and formation of fine wires may become difficult.

[0029] Further, the BET specific surface area of the flake-shaped powder is preferably within the range of 0.1 to 1 m^2/g as mentioned above, but it is more preferably within the range of 0.2 to 0.8 m^2/g , and still more preferably within the range of 0.2 to 0.5 m^2/g . If the BET specific surface area of the flake-shaped

powder is less than $0.1 \text{ m}^2/\text{g}$, there is a possibility that the contact area among particles of the conductive powder tends to decrease, resulting in failure to obtain sufficient conductivity because the flake thickness is too large and the shape of the flake-shaped powder becomes close to spheres. On the other hand, if the BET specific surface area exceeds $1 \text{ m}^2/\text{g}$, the contact area among particles of the conductive powder is increased, but the paste viscosity also increases, so that the conductive powder tends to be hardly highly filled (i.e., it is difficult to increase the content of the conductive powder in the conductive paste composition). Thus, sufficient conductivity may not be obtained.

[0030] Moreover, the tap density of the flake-shaped powder is preferably within the range of 3 to 7 g/cm^3 as mentioned above, but it is more preferably within the range of 3 to 6 g/cm^3 , and still more preferably within the range of 3.5 to 5.5 g/cm^3 . If the tap density of the flake-shaped powder is less than 3 g/cm^3 , the flake-shaped powder becomes bulky and tends to be hardly highly filled, and thus, sufficient conductivity may not be obtained. On the other hand, if the tap density exceeds 7 g/cm^3 , it is usually difficult to produce a flake-shaped powder industrially.

[0031] The aspect ratio of the flake-shaped powder is preferably within the range of 5 to 15 as mentioned above, but it is more preferably within the range of 6 to 12 and still more preferably within the range of 6 to 10. If the aspect ratio of the flake-shaped powder is less than 5, the contact area among particles of the conductive powder tends to become smaller because of insufficient flake formation. As a result, sufficient conductivity may not be obtained. On the other hand, if the aspect ratio exceeds 15, the contact area among particles of the conductive powder is increased, but such powder tends to be hardly highly filled. Thus, sufficient conductivity may not be obtained.

[0032] Methods for producing the flake-shaped powder are not particularly limited, and known methods may be used for such purpose. More specifically, for example, it is possible to produce a flake-shaped powder by subjecting a spherical powder (described later) as an original powder produced by a known method to known mechanical processing. The physical properties such as particle size and degree of aggregation of the original powder may be appropriately selected according to the intended use of the conductive paste composition (kinds of electrodes, wires, and the like, or kinds of electronic components, electronic device, and the like to be provided with such electrodes, wire, and the like).

[0033] Next, a preferred constitution of the spherical powder among the species of the conductive

powder (A) in the present invention is specifically described. The spherical powder preferably has an average particle size D50 within the range of 0.1 to 10 μm , a BET specific surface area within the range of 0.5 to 1.7 m^2/g , a tap density of 1.5 to 5 g/cm^3 , and a degree of aggregation D50/DSEM within the range of 2 to 15.

[0034] More specifically, the average particle size D50 of the spherical powder is preferably within the range of 0.1 to 10 μm as mentioned above, but it is more preferably within the range of 1 to 5 μm , and still more preferably within the range of 1 to 3 μm . If the average particle size D50 of the spherical powder is smaller than 0.1 μm , the heat-curable conductive paste becomes highly viscous, which may cause a difficulty in paste formation. On the other hand, if the average particle size D50 is larger than 10 μm , the mesh screen may be clogged and formation of fine wires may become difficult when printing a conductor pattern using a mesh screen in the same manner as in the flake-shaped powder.

[0035] Further, the BET specific surface area of the spherical powder is preferably within the range of 0.5 to 1.7 m^2/g as mentioned above, more preferably within the range of 0.6 to 1.6 m^2/g , and still more preferably within the range of 0.9 to 1.6 m^2/g . If the BET specific surface area of the spherical powder is less than 0.5 m^2/g , the contact area among particles of the conductive powder (A) tends to become smaller, so that sufficient conductivity may not be obtained. On the other hand, if the BET specific surface area exceeds 1.7 m^2/g , the contact area among particles of the conductive powder (A) is increased, but the paste viscosity also increases, so that the conductive powder tends to be hardly highly filled. As a result, sufficient conductivity may not be obtained.

[0036] Moreover, the tap density of the spherical powder is preferably within the range of 1.5 to 5 g/cm^3 as mentioned above, more preferably within the range of 2 to 5 g/cm^3 , and still more preferably within the range of 3 to 4 g/cm^3 . If the tap density of the spherical powder is less than 1.5 g/cm^3 , the conductive powder (A) becomes highly bulky and tends to be hardly highly filled. Thus, sufficient conductivity may not be obtained. On the other hand, if the tap density exceeds 5 g/cm^3 , the spherical powder becomes too dispersible, so that a resin component easily creeps among particles of the conductive powder (A), resulting in a tendency that the interface resistance among particles of the conductive powder (A) is increased. As a result, sufficient conductivity may not be obtained.

[0037] In addition, the degree of aggregation D50/DSEM of the spherical powder is preferably within

the range of 2 to 15 as mentioned above, more preferably within the range of 3 to 11, and still more preferably within the range of 3 to 7.5. If the degree of aggregation D50/DSEM of the spherical powder is smaller than 2, the spherical powder becomes too dispersible, so that a resin component easily creeps among particles of the conductive powder (A), resulting in a tendency that the interface resistance among particles of the conductive powder (A) is increased. As a result, sufficient conductivity may not be obtained. On the other hand, if the degree of aggregation D50/DSEM of the spherical powder is larger than 15, the conductive powder (A) becomes highly bulky and tends to be hardly highly filled. Thus, sufficient conductivity may not be obtained.

[0038] The production method of the spherical powder is not particularly limited, and in this embodiment, for example, those produced by a wet reduction method can be suitably used. However, spherical powders produced by known methods such as an electrolytic method and an atomization method can also be used.

[0039] [(B) Heat-Curable Resin]

Known components used in the field of heat-curable conductive paste compositions can be suitably used as the heat-curable resin (B) that is used in the heat-curable conductive paste composition according to the present invention. Typical examples of the components include (B1) an epoxy resin and (B2) a blocked polyisocyanate compound. In order to achieve a good conductor resistance, it is preferred that the heat-curable conductive paste composition contains (B2) a blocked polyisocyanate compound, or (B1) an epoxy resin and (B2) a blocked polyisocyanate compound as the heat-curable resin (B).

[0040] When the epoxy resin (B1) and the blocked polyisocyanate compound (B2) are used as the heat-curable resin (B), they are preferably used in a predetermined blending ratio as described below.

[0041] The specific kind and structure of the epoxy resin (B1) are not particularly limited, but a polyvalent epoxy resin having two or more oxirane rings (epoxy groups) in the molecule is preferable. Examples thereof include glycidyl ether type epoxy resins obtained by reacting epichlorohydrin with a polyhydric phenol (e.g. novolac such as phenol novolac and cresol novolac, bisphenol A, hydrogenated bisphenol A, bisphenol F, bisphenol AD, and resorcin) or a polyhydric alcohol (e.g. ethylene glycol, neopentyl glycol, glycerin, trimethylolpropane, pentaerythritol, triethylene glycol, and polypropylene

glycol); glycidyl amine type epoxy resins obtained by reacting epichlorohydrin with a polyamino compound (e.g. ethylenediamine, triethylenetetramine, and aniline); glycidyl ester type epoxy resins obtained by reacting epichlorohydrin with a polyvalent carboxylic compound (e.g., adipic acid, phthalic acid, and isophthalic acid); and alicyclic type epoxy resins synthesized by, for example, the oxidation of an olefin. These epoxy resins may be used alone or in combination.

[0042] Further, known compounds in the field of heat-curable conductive pastes can be preferably used as the blocked polyisocyanate compound (B2).

[0043] More specifically, examples of the blocked polyisocyanate compound (B2) include aromatic isocyanates (e.g. tolylene diisocyanate, diphenylmethane diisocyanate, polymethylene polyphenyl polyisocyanate, tolidine diisocyanate, xylylene diisocyanate, and naphthalene diisocyanate); and aliphatic polyisocyanates (e.g. hexamethylene diisocyanate, isophorone diisocyanate, hydrogenated xylylene diisocyanate, dicyclohexylmethane diisocyanate, octamethylene diisocyanate, and trimethylhexamethylene diisocyanate). These polyisocyanate compounds may be used alone or may be used in combination of two or more thereof as appropriate. Further, among these polyisocyanate compounds, tri- or more nuclear polymethylene polyphenyl polyisocyanate is more preferably used.

[0044] Further, in the present embodiment, a terminal isocyanate group-containing compound synthesized by reacting a known polyisocyanate with a known polyol by a known method can also be suitably used as the polyisocyanate compound in the present invention. There is no particular limitation on the polyol used in this case, and general polyether polyols, polyester polyols, polycarbonate polyols and the like can be suitably used.

[0045] The blocked polyisocyanate compound (B2) in the present invention is a compound obtained by blocking the polyisocyanate compound described above. The blocking agent for the polyisocyanate compound is not particularly limited, and it is possible to suitably use imidazoles, phenols, oximes, and the like.

[0046] When the epoxy resin (B1) and the blocked polyisocyanate compound (B2) are used in combination as the heat-curable resin (B) in the heat-curable conductive paste according to the present invention, the mixing ratio (blending ratio) between them is not particularly limited, and it is preferable to blend B1 and B2 within the range of B1 : B2 = 0 : 100 to 90 : 10 (excluding 0 : 100), more preferably

within the range of 10 : 90 to 80 : 20 by mass ratio.

[0047] If the amount of the epoxy resin (B1) is 90 parts by mass or less, i.e. if the amount of the blocked polyisocyanate compound (B2) is 10 parts by mass or more when the total amount of the epoxy resin (B1) and the blocked polyisocyanate compound (B2) is 100 parts by mass, an effect of promoting the contact among particles of the conductive powder (A) is large due to the curing shrinkage of the blocked polyisocyanate compound (B2). This is desirable because sufficient conductivity is obtained.

[0048] The content of the heat-curable resin (B) is not particularly limited, but in this embodiment, the content of the heat-curable resin (B) is preferably within the range of 1 to 40 parts by mass, more preferably within the range of 1 to 30 parts by mass, and still more preferably within the range of 1 to 20 parts by mass, relative to 100 parts by mass of the conductive powder (A). When the content of the heat-curable resin (B) is 1 part by mass or more, adhesion to the substrate is good, and whereas when the content of the heat-curable resin (B) is 40 parts by mass or less, it is desirable because sufficient conductivity is obtained.

[0049] Further, the heat-curable conductive paste according to the present invention may contain other known resins as a binder resin, in addition to the epoxy resin (B1) and the blocked polyisocyanate compound (B2) as the heat-curable resin (B). Examples of the resins usable as the binder resin include, but not limited to, phenol resins, polyester resins, polyurethane resins, acrylic resins, melamine resins, polyimide resins, and silicone resins.

[0050] [(C) Curing Agent]

The curing agent (C) used in the heat-curable conductive paste according to the present invention is not particularly limited as long as it is a compound capable of curing the heat-curable resin (B). In this embodiment, since the blocked polyisocyanate compound (B2), or the epoxy resin (B1) and the blocked polyisocyanate compound (B2) are preferably contained as the heat-curable resin (B), the type of the curing agent (C) is not limited as long as it cures at least the epoxy resin (B1) or the blocked polyisocyanate compound (B2), and includes various known compounds in the field of heat-curable conductive pastes.

[0051] Specifically, examples of the curing agent (C) includes acid anhydrides (e.g. phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, maleic anhydride, tetrahydrophthalic anhydride,

methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, methylhexahydrophthalic anhydride, and succinic anhydride); imidazoles (e.g. imidazole, 2-methylimidazole, 2-ethyl-4-methylimidazole, 2-undecyl imidazole, 2-heptadecylimidazole, 1-benzyl-2-methylimidazole, 2-phenyl-4-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-aminoethyl-2-methylimidazole, 1-methylimidazole, and 2-ethyl imidazole); tertiary amines (e.g. 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 a boron fluoride (e.g. boron trifluoride ethyl ether, boron trifluoride phenol, boron trifluoride piperidine, boron trifluoride acetic acid, boron trifluoride monoethylamine, boron trifluoride triethanolamine, and boron trifluoride monoethanolamine) or a compound thereof; amine adducts (e.g. Amicure series PN-23 and MY-24, commercially available from Ajinomoto Fine-Techno Co., Inc., and Fujicure series FXR-1020 and FXR-1030, commercially available from Fuji Kasei Kogyo Co., Ltd.); and dicyandiamides. These compounds may be used alone or may be used in an appropriate combination of two or more thereof.

[0052] The amount of the curing agent (C) added is not particularly limited, and in this embodiment, it is preferably within the range of 1 to 30 parts by mass, more preferably within the range of 1 to 15 parts by mass, still more preferably within the range of 1 to 10 parts by mass, relative to 100 parts by mass of the heat-curable resin (B). If the amount of the curing agent (C) added is less than 1 part by mass, there is a possibility that the curing of the heat-curable resin (B) may be insufficient, as well as a possibility that good conductivity of the cured product (electrodes, wires, etc.) cannot be obtained. On the other hand, if the amount of the curing agent (C) added exceeds 30 parts by mass, there is a possibility that the paste viscosity increases, and such a case is not preferable in terms of cost.

[0053] [(D) Inorganic ion exchanger]

The inorganic ion exchanger (C) used in the heat-curable conductive paste composition according to the present invention is not particularly limited as long as it can capture copper ions in the heat-curable conductive paste composition, but the inorganic ion exchanger (C) preferably contains any one of zirconium, magnesium, aluminum, silicon, antimony, and bismuth as a main component.

[0054] In the present invention, the main component of the inorganic ion exchanger (D) refers to one that is contained in an amount of 50% by mass or more among the components constituting the inorganic ion exchanger (D).

[0055] Specific examples of the inorganic ion exchanger (D) include cation exchange type or amphoteric ion exchange type of IXEPLAS series and IXE series commercially available from Toagosei Co., Ltd. (IXEPLAS A-1, A-2, and B-1, and IXE-100, 300, 600, 633, 6107, and 6136), and cation exchange type or amphoteric ion exchange type of Kyoward series commercially available from Kyowa Hakko Kogyo Co., Ltd. (e.g. Kyoward 600, 700, 1000, and 2000). These inorganic ion exchangers may be used alone or in an appropriate combination of two or more thereof.

[0056] In the present invention, it is preferable that the heat-curable conductive paste composition contains the inorganic ion exchanger (D) in an amount of 0.01 to 3% by mass, more preferably in an amount of 0.02 to 2% by mass, still more preferably in an amount of 0.03 to 1% by mass, relative to the conductive powder (A). If the content of the inorganic ion exchanger (D) is 0.01% by mass or more, copper ions can be sufficiently captured and more superior storage stability can be achieved. If the content of the inorganic ion exchanger (D) is 3% by mass or less, it is desirable because sufficient conductivity can be obtained.

[0057] [Production of Heat-Curable Conductive Paste Composition]

The method for producing a heat-curable conductive paste composition according to the present invention is not particularly limited, and methods known in the field of heat-curable conductive pastes may be suitably used. As a typical example, there is a method of mixing the above components in a predetermined mixing ratio (by mass) and forming the mixture into a paste by using a known kneading apparatus. As the kneading apparatus, for example, a three-roll mill can be mentioned.

[0058] In addition, the heat-curable conductive paste according to the present invention may contain, if necessary, various known additives in the field of heat-curable conductive pastes, other than the components mentioned above (the conductive powder (A), the heat-curable resin (B), the curing agent (C), and the inorganic ion exchanger (D)). Such additives are not particularly limited, and specific examples thereof include dispersing agents, leveling agents, antioxidants, ultraviolet absorbers, silane coupling agents, anti-foaming agents, and viscosity modifiers. These additives may be added as long as

the effect of the present invention is not impaired.

[0059] Further, the method of forming a conductor pattern by the heat-curable conductive paste composition according to the present invention is not particularly limited, and various known methods may be suitably used. Typically, as shown in examples described later, such a method includes a screen printing method. Although the heat-curable conductive paste composition is particularly suitably used for the formation of the conductor pattern by the screen printing method, the present invention is not limited only to this printing method, but may be applied to other printing methods such as an ink-jet method and a dispenser method.

[Application of Heat-Curable Conductive Paste Composition]

The heat-curable conductive paste according to the present invention can be widely used for the formation of highly fine electrodes and wires. More specifically, for example, the heat-curable conductive paste can be suitably used for solar cell collecting electrodes; external electrodes of chip-type electronic components; and electrodes or wires of components used for RFID (Radio Frequency Identification), electromagnetic wave shielding, vibrator adhesion, membrane switches, or electroluminescence. Among these applications, one particularly preferred application may be a solar cell collecting electrode.

Examples

[0060] The present invention will be more specifically described with reference to examples, comparative examples, and reference examples, but is not limited thereto. Various changes, alterations, and modifications may be made thereto by those skilled in the art without departing from the scope of the present invention. It is to be noted that various synthetic reactions and measurement/evaluation of physical properties in the following examples were performed in the following manner.

[0061] (Measurement /Evaluation Method)

[Evaluation Method for Conductive Powder]

(1) Average Particle size D50

The average particle size D50 of the flake-shaped powder and the spherical powder was evaluated by a laser diffraction method. Into a 50-ml beaker, 0.3 g of a sample of the flake-shaped

powder or the spherical powder was weighed, and 30 ml of isopropyl alcohol was added thereto. Then, the mixture was dispersed by treatment for 5 minutes using an ultrasonic cleaner (USM-1, manufactured by AS ONE Corporation). The average particle size D50 was measured using a microtrac particle size distribution analyzer (9320-HRA X-100, manufactured by Nikkiso Co., Ltd.) and then evaluated.

[0062] (2) Evaluation of BET Specific Surface Area

The BET specific surface area of the flake-shaped powder or the spherical powder was measured and evaluated by nitrogen adsorption of 1 g of a sample using MONOSORB (manufactured by Quanta Chrome Corporation) by a BET one-point method. Note that in the BET specific surface area measurement, degassing conditions before the measurement were 10 minutes at 60°C.

[0063] (3) Evaluation of Tap Density

The tap density of the flake-shaped powder or the spherical powder was evaluated by using a tap density measuring device (bulk density measuring device SS-DA-2, manufactured by Shibayama Scientific Co., Ltd.). That is, 15 g of a sample was weighed, placed in a 20-ml test tube, tapped 1000 times with a drop of 20 mm, and evaluated by calculating the tap density according to the following equation.

[0064] $\text{Tap density} = \text{Sample mass (15 g)} / \text{Sample volume after tapping (cm}^3\text{)}$

[Measurement of Paste Viscosity]

The paste viscosity of the heat-curable conductive paste composition was measured using a viscometer DV-III manufactured by Brookfield Corp. Using CP-52 as a cone in the measurement, the paste viscosity (η 1rpm) at the rotation rate of 1 rpm (shear rate 2s⁻¹) was measured.

[0065] [Measurement of Conductor Resistance]

An alumina substrate was used as the base material. Then, as shown in Fig. 1, a conductor pattern 11 having a terminal 11a and a terminal 11b on both ends, respectively, and a wire part 11c that is zigzag-shaped was screen-printed on the surface of the alumina substrate, using the heat-curable conductive paste composition of any of examples and comparative examples. Thereafter, the alumina substrate was heated in a hot-air dryer of 180°C for 60 minutes to cure the conductor pattern 11 (heat-curable conductive paste composition), whereby a conductor resistance evaluation sample was prepared.

[0066] With respect to the conductor resistance evaluation sample of each of examples and comparative examples, the thickness of the conductor pattern 11 was measured by a surface roughness meter (Surfcom 480A, manufactured by Tokyo Seimitsu Co., Ltd.), and the electric resistance was measured by a digital multi-meter (R6551, manufactured by Advantest Corp.). Based on the film thickness, electric resistance, and the aspect ratio of the wiring pattern, the conductor resistance was calculated and evaluated.

[0067]

[Table 1]

	Shape	Average particle size (μm)	Specific surface area (m^2/g)	Tap density (g/cm^3)	Content of silver coating (%)
Silver (1)	Spherical	1.1	1.5	3.5	-
Silver (2)	Flake-shaped	5.7	0.5	4.5	-
Copper (1)	Spherical	3.0	0.4	4.3	-
Copper (2)	Spherical	5.6	0.3	4.4	-
Copper alloy	Spherical	4.3	0.3	3.8	-
Silver-coated copper (1)	Spherical	2.9	0.5	4.0	7.5
Silver-coated copper (2)	Spherical	5.3	0.3	4.5	10.2
Silver-coated copper (3)	Spherical	8.0	0.2	4.0	15.1
Silver-coated copper alloy	Spherical	4.4	0.3	3.9	10.0

[0068]

[Table 2]

		Compound name
Epoxy resin (1)	E-1	Bisphenol A type epoxy resin [Mitsubishi Chemical Corporation, Product name jER825, epoxy equivalent: 170 to 180]
Epoxy resin (2)	E-2	Phenol novolac type epoxy resin [Mitsubishi Chemical Corporation, Product name jER152, epoxy equivalent: 172 to 178]
Blocked polyisocyanate compound (1)	U-1	Reaction compound of polymethylene polyphenyl polyisocyanate with polycarbonate polyol [Blocking agent: methylethylketone oxime]
Blocked polyisocyanate compound (2)	U-2	Reaction compound of isocyanurate type polyisocyanate of hexamethylene diisocyanate with polypropylene polyol [Blocking agent: methylethylketone oxime]
Curing agent (1)	H-1	Boron trifluoride monoethylamine
Curing agent (2)	H-2	2-Ethyl-4methylimidazole

[0069]

[Table 3]

	(A) Conductive powder		(B) Heat-curable resin		(C) Curing agent	(D) Inorganic ion exchanger	
	Kind	Blending ratio (% by mass)	Kind	Blending ratio (% by mass)		Kind	Blending ratio (% by mass)
Example 1	Copper (1)	100	U-1	100	H-1	IXE-100	0.1
Example 2	Silver-coated copper (1)	100	U-2	100	H-2	IXEPLAS A-2	0.05
Example 3	Silver-coated copper alloy	100	U-1	100	H-1	IXEPLAS A-1	0.1
Example 4	Silver (1)/Copper (1)	50/50	U-2	100	H-2	IXEPLAS A-2	0.05
Example 5	Silver (1)/silver (2)/silver-coated copper (2)	25/25/50	U-1	100	H-1	IXEPLAS A-1	0.1
Example 6	Copper (1)	100	U-1/E-1	70/30	H-1	Kyoward 1000	0.02
Example 7	Silver-coated copper (1)	100	U-1/E-2	70/30	H-2	IXEPLAS A-2	0.02
Example 8	Silver (1)/Copper (2)	50/50	U-2/E-1	70/30	H-1	Kyoward 2000	0.1
Example 9	Silver (1)/silver (2)/silver-coated copper (2)	10/10/80	U-2/E-2	70/30	H-2	IXEPLAS A-2	0.1
Example 10	Copper (2)	100	U-1/E-1	50/50	H-1	IXE-300	0.5
Example 11	Silver-coated copper (3)	100	U-1/E-2	50/50	H-2	IXE-600	0.5
Example 12	Copper alloy	100	U-2/E-1	50/50	H-1	Kyoward 600	0.5
Example 13	Silver (2)/silver-coated copper (1)	50/50	U-2/E-2	50/50	H-2	Kyoward 700	0.5
Example 14	Silver (1)/silver (2)/silver-coated copper (2)	25/25/50	U-1/E-1	50/50	H-1	IXEPLAS A-1	0.5
Example 15	Silver-coated copper (1)	100	U-1/E-1	10/90	H-1	IXEPLAS A-1	1
Example 16	Silver (1)/ Silver-coated copper alloy	10/90	U-1/E-2	10/90	H-2	IXEPLAS A-2	1
Example 17	Silver (1)/Silver (2)/Silver-coated copper (2)	10/10/80	U-2/E-1	10/90	H-1	IXE-633	1
Example 18	Silver (1)/Silver-coated copper (3)	30/70	U-2/E-2	10/90	H-2	IXEPLAS B-1	3
Comparative Example 1	Copper (1)	100	U-1	100	H-1	-	-
Comparative Example 2	Silver-coated copper (1)	100	U-1/E-1	50/50	H-1	-	-
Comparative Example 3	Silver-coated copper alloy	100	U-1/E-2	50/50	H-2	-	-
Comparative Example 4	Silver (1)/Silver-coated copper (2)	50/50	U-2/E-1	50/50	H-1	-	-
Comparative Example 5	Silver (1)/Silver-coated copper alloy	50/50	U-2/E-2	50/50	H-2	-	-
Comparative Example 6	Silver (1)/Silver (2)/ silver-coated copper (2)	25/25/50	U-1/E-1	50/50	H-1	IXEPLAS A-1	5
Reference Example 1	Silver (1)	100	U-1	100	H-2	-	-
Reference Example 2	Silver (1)/Silver (2)	50/50	U-1/E-1	10/90	H-1	-	-

[0070] (Examples 1 to 18) (Comparative Examples 1 to 6) (Reference Examples 1 to 2)

[Production Method of Heat-Curable Conductive Paste Composition]

Using the conductive powder (A) shown in Table 1, the heat-curable resin (B) and the curing agent (C) shown in Table 2, and the inorganic ion exchanger (D), a heat-curable conductive paste composition was prepared by blending the conductive powder (A)/the heat-curable resin (B)/the curing agent (C) in a blending ratio by mass of 90/10/0.5, adding thereto the inorganic ion exchanger (D) in a blending ratio shown in Table 3 relative to the conductive powder (A), kneading the mixture with a three roll mill, and adding butyl diglycol acetate thereto to adjust the viscosity of the paste to 100 Pa·s (1 rpm).

[0071] In Table 1, the copper alloy is an alloy obtained by adding nickel and zinc to copper.

[0072] For the obtained heat-curable conductive paste composition, the initial conductor resistance, and the viscosity and the conductor resistance after 3 days storage at 30°C, and the viscosity and the conductor resistance after 3 months storage at 0°C were measured. The results are shown in Table 4.

[0073] The viscosity and the conductor resistance after the lapse of a predetermined storage period shown in Table 4 indicate a relative value with the viscosity and the conductor resistance immediately after preparation of the heat-curable conductive paste composition each taken as 1.0.

[0074]

[Table 4]

	Initial conductor resistance ($\mu\Omega\cdot\text{cm}$)	30°C, 3 days storage		0°C, 3 months storage	
		Viscosity	Conductor resistance	Viscosity	Conductor resistance
Example 1	260	1.0	1.0	1.0	1.0
Example 2	80	1.0	1.0	1.0	1.0
Example 3	90	1.0	1.0	1.0	1.0
Example 4	132	1.0	1.0	1.0	1.0
Example 5	40	1.0	1.0	1.0	1.0
Example 6	270	1.1	1.0	1.0	1.0
Example 7	90	1.1	1.0	1.0	1.0
Example 8	90	1.0	1.0	1.0	1.0
Example 9	60	1.0	1.0	1.0	1.0
Example 10	190	1.0	1.0	1.0	1.0
Example 11	130	1.0	1.0	1.0	1.0
Example 12	240	1.0	1.0	1.0	1.0
Example 13	60	1.0	1.0	1.0	1.0
Example 14	40	1.0	1.0	1.0	1.0
Example 15	100	1.0	1.0	1.0	1.0
Example 16	90	1.0	1.0	1.0	1.0
Example 17	70	1.0	1.0	1.0	1.0
Example 18	100	1.0	1.0	1.0	1.0
Comparative Example 1	260	2.4	1.7	1.8	1.5
Comparative Example 2	100	2.0	1.4	1.6	1.3
Comparative Example 3	100	2.0	1.4	1.6	1.3
Comparative Example 4	40	1.7	1.3	1.4	1.2
Comparative Example 5	50	1.7	1.3	1.4	1.2
Comparative Example 6	70	1.0	1.0	1.0	1.0
Reference Example 1	10	1.0	1.0	1.0	1.0
Reference Example 2	20	1.0	1.0	1.0	1.0

[0075] Comparing the results of Examples 1 to 18 with those of Comparative Examples 1 to 5, the viscosities and the conductor resistances of Examples 1 to 18 are each 1.0 or 1.1, and the viscosities of Comparative Examples 1 to 5 are all 1.4 or more and the conductor resistances of Comparative Examples 1 to 5 are all 1.2 or more. It is found that when the heat-curable conductive paste composition contains the inorganic ion exchanger (D), changes in the viscosity and the conductor resistance of the heat-curable conductive paste containing copper, silver-coated copper, a copper alloy or a silver-coated copper alloy as the conductive powder (A) are small and good results are obtained.

[0076] As described above, according to the present invention, it becomes possible to provide a heat-curable conductive paste composition preventing an increase of viscosity and a decrease in conductivity during its storage and having superior storage stability by using the inorganic ion exchanger (D) even when using copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy as the conductive powder.

[0077] Note that the present invention is not intended to be limited to the description of the above embodiment, but may be altered in many ways within the scope shown in the claims, and embodiments obtained by appropriately combining technical means disclosed in different examples and plural modifications are also included in the technical scope of the present invention.

Industrial Applicability

[0078] The present invention can be suitably used in the field of producing various electronic devices and electronic components, in particular, in the field where it is required to form a more highly fine electrodes and wires, such as solar cell collecting electrodes, external electrodes of chip-type electronic components, and electrodes or wires of components used for RFID, electromagnetic wave shielding, vibrator adhesion, membrane switches, or electroluminescence.

Reference Signs List

[0079] 11 Conductor pattern
 11a Terminal
 11b Terminal

11c Wire part

CLAIMS

1. A heat-curable conductive paste composition comprising: (A) a conductive powder, (B) a heat-curable resin, (C) a curing agent, and (D) an inorganic ion exchanger, wherein
at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy is used as the conductive powder (A), and
a blocked polyisocyanate compound, or a blocked polyisocyanate compound and an epoxy resin are contained as the heat-curable resin (B).
2. The heat-curable conductive paste composition according to claim 1, wherein the inorganic ion exchanger (D) contains any one of zirconium, magnesium, aluminum, silicon, antimony, and bismuth as a main component.
3. The heat-curable conductive paste composition according to claim 1 or 2, wherein the content of the inorganic ion exchanger (D) is 0.01 to 3% by mass relative to the conductive powder (A).
4. The heat-curable conductive paste composition according to any one of claims 1 to 3, wherein
at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy, and silver are used as the conductive powder (A), and
the blending ratio by mass of the at least one member selected from the group consisting of copper, a copper alloy, silver-coated copper, and a silver-coated copper alloy to silver is 100 : 0 to 1 : 99 (excluding 100 : 0).
5. The heat-curable conductive paste composition according to any one of claims 1 to 4, wherein
at least one member selected from the group consisting of gold, palladium, nickel, aluminum, lead, and carbon is further contained as the conductive powder (A).