DESCRIPTION

TITLE OF INVENTION: SILVER-COATED RESIN PARTICLE AND FILLER-CONTAINING PASTE

TECHNICAL FIELD

[0001] The present invention relates to a silver-coated resin particle and a filler-containing paste.

Priority is claimed on Japanese Patent Application No. 2024-034043, filed March 6, 2024, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002] For example, conductive adhesives such as a conductive paste and a conductive film, in which silver-coated resin particles obtained by coating resin particles with silver are mixed with a resin, are known as conductive materials that replace lead solder or lead-free solder. The conductive adhesives are used, for example, as forming materials for electrodes, electrical wiring, and the like, which constitute electronic devices such as a solar cell panel, a liquid crystal display, and a touch panel.

In addition, pastes, films, and the like in which the above-described silver-coated resin particles and a resin are mixed are also used as thermal interface materials (TIM) because they also have excellent thermal conductivity.

[0003] As the above-described silver-coated resin particles, for example, Patent Document 1 discloses silver-coated resin particles in which adhesion between resin particles and a silver coating layer is enhanced by subjecting resin particles to a catalyzing treatment using tin as a pretreatment and subjecting the pretreated resin particles to electroless silver plating.

Citation List

Patent Document

[0004] Patent Document 1: Japanese Unexamined Patent Application, First Publication No. 2015-199970

SUMMARY OF INVENTION

Technical Problem

[0005] Recently, semiconductor elements for power electronics used for high-power control of wind power generation, electric vehicles, hybrid vehicles, and the like generate a large amount of heat during operation and have a large area. Therefore, when such semiconductor elements are bonded, high bonding reliability needs to be ensured even under a thermal cycle load.

Accordingly, in a filler-containing paste containing the above-described silver-coated resin particles as a filler, silver-coated resin particles having particularly excellent adhesion between resin particles and a silver coating layer are required in order to improve thermal cycle reliability of a bonding layer.

[0006] The present invention has been made in view of the above-described circumstances, and an objective thereof is to provide a silver-coated resin particle having excellent adhesion between a resin particle and a silver coating layer and having excellent thermal cycle resistance, and a filler-containing paste containing the silver-coated resin particle as a filler.

Solution to Problem

[0007] As a result of intensive studies conducted by the present inventors in order to solve the above-described problems, the present inventors have found that, when a large amount of tin used as a pretreatment (catalyzing treatment) for plating is contained, a silver coating layer is likely to peel off under a thermal cycle load, so that it is necessary

to reduce a contained amount of tin. The present inventors have also found that, by providing silicon oxide on a surface of resin particles, silver can be favorably plated on the surface of the resin particles.

[0008] The present invention has been made based on the above-described findings, and a silver-coated resin particle according to an aspect 1 of the present invention is a silver-coated resin particle including a resin particle formed of a resin composition and a silver coating layer formed on a surface of the resin particle, and is characterized in that the silver-coated resin particle contains silicon oxide in a range of 0.04% by mass or more and 3.00% by mass or less, and a contained amount of tin is 0.20% by mass or less.

[0009] With the silver-coated resin particle according to the aspect 1 of the present invention, since silicon oxide is contained in a range of 0.04% by mass or more and 3.00% by mass or less, silver can be favorably plated on the surface of the resin particle, and the amount of tin used in a catalyzing treatment can be reduced. In addition, since the contained amount of tin is limited to 0.20% by mass or less, peeling of the silver coating layer under a thermal cycle load can be suppressed.

Therefore, a silver-coated resin particle having excellent adhesion between the resin particle and the silver coating layer and having excellent thermal cycle resistance can be provided.

[0010] A silver-coated resin particle according to an aspect 2 of the present invention is characterized in that, in the silver-coated resin particle according to the aspect 1 of the present invention, a 5% compression modulus (5% K value) is 2.5 GPa or less.

With the silver-coated resin particle according to the aspect 2 of the present invention, since the 5% compression modulus (5% K value) is 2.5 GPa or less, the silver-coated resin particle is sufficiently soft and easily deformable. Therefore, for example, occurrence of cracks in a paste cured product of a paste containing the silver-coated resin

particle as a filler can be suppressed.

[0011] A silver-coated resin particle according to an aspect 3 of the present invention is characterized in that, in the silver-coated resin particle according to the aspect 1 or the aspect 2 of the present invention, the resin composition is one or more selected from an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin.

With the silver-coated resin particle according to the aspect 3 of the present invention, since the resin composition is one or more selected from the group consisting of an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin, the resin particle has excellent flexibility and is particularly suitable as a filler.

[0012] A silver-coated resin particle according to an aspect 4 of the present invention is characterized in that, in the silver-coated resin particle according to any one of the aspects 1 to 3 of the present invention, a particle diameter is in a range of 2 μm or more and 50 μm or less.

With the silver-coated resin particle according to the aspect 4 of the present invention, since the particle diameter is in a range of 2 μm or more and 50 μm or less, the amount of expensive silver used can be suppressed to reduce cost, and the silver-coated resin particle can be used as a filler for a paste or the like for forming a fine pattern.

[0013] A filler-containing paste according to an aspect 5 of the present invention is characterized by containing a binder resin and the silver-coated resin particle according to any one of the aspects 1 to 4 of the present invention as a filler.

With the filler-containing paste according to the aspect 5 of the present invention, since the filler-containing paste contains the silver-coated resin particle according to any one of the aspects 1 to 4 of the present invention as a filler, thermal cycle reliability of a cured product of the filler-containing paste can be improved, and the filler-containing paste can be stably used as a conductive adhesive or a heat transfer material even in applications in

which a severe thermal cycle is applied.

Advantageous Effects of Invention

[0014] According to the present invention, it is possible to provide a silver-coated resin particle having excellent adhesion between a resin particle and a silver coating layer and having excellent thermal cycle resistance, and a filler-containing paste containing the silver-coated resin particle as a filler.

BRIEF DESCRIPTION OF DRAWINGS

[0015] [FIG. 1] A cross-sectional view of a silver-coated resin particle according to an embodiment of the present invention.

[FIG. 2] A flowchart representing a method for producing a silver-coated resin particle according to an embodiment of the present invention.

[FIG. 3] An explanatory diagram of a semiconductor device using a paste cured product according to an embodiment of the present invention.

[FIG. 4A] A photograph showing a result of SEM observation of a silver-coated resin particle of Inventive Example 1 in Examples.

[FIG. 4B] A photograph showing a result of SEM observation of a silver-coated resin particle of Inventive Example 1 in Examples.

[FIG. 5] A photograph showing a result of SEM observation of a silver-coated resin particle of Inventive Example 6 in Examples.

[FIG. 6A] A photograph showing a result of SEM observation of a silver-coated resin particle of Comparative Example 5 in Examples.

[FIG. 6B] A photograph showing a result of SEM observation of a silver-coated resin particle of Comparative Example 5 in Examples.

[FIG. 7] A photograph showing a result of SEM observation of a silver-coated resin particle of Comparative Example 6 in Examples.

DESCRIPTION OF EMBODIMENTS

[0016] Hereinafter, a silver-coated resin particle and a filler-containing paste according to an embodiment of the present invention will be described with reference to the accompanying drawings. Note that each of the embodiments shown below is specifically described for better understanding of the gist of the invention, and does not limit the present invention unless otherwise specified.

[0017] FIG. 1 shows a silver-coated resin particle 10 according to an embodiment of the present invention. For example, the silver-coated resin particle 10 according to the present embodiment includes, as shown in FIG. 1, a resin particle 11 formed of a resin composition and a silver coating layer 12 formed on a surface of the resin particle 11.

The silver-coated resin particle 10 contains silicon oxide in a range of 0.04% by mass or more and 3.00% by mass or less, and a contained amount of tin is 0.20% by mass or less.

[0018] Here, in the present embodiment, the contained amount of silicon oxide in the silver-coated resin particle 10 is calculated by collecting a measurement sample from the silver-coated resin particle 10, performing elemental analysis, and converting the measured Si contained amount to a silicon oxide (SiO_2) equivalent.

In addition, the contained amount of tin in the silver-coated resin particle 10 is the measured tin amount obtained by collecting a measurement sample from the silver-coated resin particle 10 and performing elemental analysis.

[0019] In addition, in the silver-coated resin particle 10 according to the present embodiment, it is preferable that a 5% compression modulus (5% K value) is 2.5 GPa or less.

In addition, in the silver-coated resin particle 10 according to the present embodiment, it is preferable that a particle diameter is in a range of 2 μm or more and 50 μm or less.

In addition, in the silver-coated resin particle 10 according to the present embodiment, it

is preferable that the resin composition constituting the resin particle 11 is one or more selected from an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin.

In the silver-coated resin particle 10 according to the present embodiment, since the flexibility is imparted, the interference effect against expansion and shrinkage is increased, so that it is more preferable to use a urethane resin or an acrylic resin having particularly excellent flexibility.

[0020] The reasons why the silver-coated resin particle 10 according to the present embodiment is defined as described above will be described below.

[0021] (Silicon oxide)

In the silver-coated resin particle 10 according to the present embodiment, by containing silicon oxide (for example, SiO2, a compound made of silicon and oxygen represented by SiO2, or the like), it is possible to favorably plate silver on the surface of the resin particle 11, thereby improving adhesion between the resin particle 11 and the silver coating layer 12.

Here, when the contained amount of silicon oxide in the silver-coated resin particle 10 is less than 0.04% by mass, there is a possibility that the adhesion between the resin particle 11 and the silver coating layer 12 cannot be sufficiently improved. On the other hand, when the contained amount of silicon oxide is more than 3.00% by mass, there is a possibility that the flexibility of the silver-coated resin particle 10 is reduced.

For this reason, in the silver-coated resin particle 10 according to the present embodiment, the contained amount of silicon oxide is set in a range of 0.04% by mass or more and 3.00% by mass or less.

[0022] In order to further improve the adhesion between the resin particle 11 and the silver coating layer 12, the contained amount of silicon oxide in the silver-coated resin

particle 10 is preferably 0.10% by mass or more, and more preferably 0.20% by mass or more.

In addition, in order to further ensure the flexibility of the silver-coated resin particle 10, the contained amount of silicon oxide in the silver-coated resin particle 10 is preferably 3.00% by mass or less, and more preferably 2.00% by mass or less.

[0023] (Contained amount of tin)

In the silver-coated resin particle 10 according to the present embodiment, when a catalyzing treatment using tin is performed as a pretreatment for plating the surface of the resin particle 11, tin is contained in the silver-coated resin particle 10. Here, when the contained amount of tin is more than 0.20% by mass, the silver coating layer 12 may easily peel off under a thermal cycle load.

For this reason, in the silver-coated resin particle 10 according to the present embodiment, the contained amount of tin is limited to 0.20% by mass or less.

[0024] In order to more reliably suppress peeling of the silver coating layer 12 under a thermal cycle load, the contained amount of tin in the silver-coated resin particle 10 is preferably 0.20% by mass or less, and more preferably 0.10% by mass or less.

In addition, the lower limit of the contained amount of tin in the silver-coated resin particle 10 is not limited, and the catalyzing treatment using tin may not be performed as a pretreatment for plating the surface of the resin particle 11, and the contained amount of tin may be 0.00% by mass.

[0025] (5% Compression modulus (5% K value))

In the silver-coated resin particle 10 according to the present embodiment, when the 5% compression modulus (5% K value) is 2.5 GPa or less, the flexibility of the silver-coated resin particle 10 is sufficiently ensured, so that occurrence of cracks in a paste cured product of a paste containing the silver-coated resin particle 10 as a filler can be

suppressed.

[0026] In order to further ensure the flexibility, the 5% compression modulus (5% K value) of the silver-coated resin particle 10 is more preferably 1.5 GPa or less, and still more preferably 0.5 GPa or less.

In addition, the lower limit of the 5% compression modulus (5% K value) of the silver-coated resin particle 10 is not particularly limited, but from the viewpoint of shape stability of the paste cured product, the 5% compression modulus is preferably 0.2 GPa or more, and more preferably 0.3 GPa or more.

[0027] (Particle diameter)

In the silver-coated resin particle 10 according to the present embodiment, when the particle diameter is 2 μm or more, a specific surface area does not become larger than necessary, the amount of silver constituting the silver coating layer 12 can be suppressed, and the production cost can be kept low. On the other hand, in the silver-coated resin particle 10 according to the present embodiment, when the particle diameter is 50 μm or less, a paste containing the silver-coated resin particle 10 as a filler can be applied in a fine pattern, and can be applied to a semiconductor device or the like having a high degree of integration or a high degree of precision.

[0028] In order to further suppress the used amount of silver constituting the silver coating layer 12, the particle diameter of the silver-coated resin particle 10 is more preferably 4 μm or more, and still more preferably 6 μm or more.

In addition, in order to accommodate an even finer pattern, the particle diameter of the silver-coated resin particle 10 is more preferably 15 μm or less, and still more preferably 10 μm or less.

[0029] (Resin composition)

In the present embodiment, when the resin composition constituting the resin particle 11

is one or more selected from an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin, the resin particle 11 has excellent flexibility, and the silver coating layer 12 can be stably formed.

[0030] Next, an example of a method for producing the silver-coated resin particle 10 according to the present embodiment will be described with reference to a flowchart of FIG. 2.

[0031] (Silicon oxide providing step S01)

First, silicon oxide is provided on the surface of the resin particle 11. Examples of a method of providing silicon oxide include a method of forming a silicate film or a silica film on the surface of the resin particle 11 (production method 1), and a method of physically attaching a silica particle to the surface of the resin particle 11 (production method 2).

[0032] As the production method 1, for example, a silicate film can be formed on the surface of the resin particle 11 by dispersing the resin particle 11 in a mixed solvent of water and ethanol, adding a predetermined amount of methyl silicate, and adding a trace amount of nitric acid or the like as a catalyst. A raw material for forming the silica film is not limited to methyl silicate, and an organic silicate such as ethyl silicate and propyl silicate, or an inorganic silicon salt such as sodium silicate can also be used.

[0033] As the production method 2, for example, a silica particle can be attached to the surface of the resin particle 11 by mixing predetermined amounts of the resin particle 11 and silica particles and subjecting the mixture to a planetary ball mill or the like. As the silica particles, those ranging from fine particles of several nm to several μm in size can be used, and those having a spherical, acicular, or beaded shape can be used.

[0034] (Catalyzing treatment step S02)

Next, tin (divalent tin ions) serving as a catalyst is adsorbed onto the resin particle 11

having silicon oxide provided on its surface.

The above-described resin particle 11 is added to an aqueous solution of a tin compound and stirred. Here, as the tin compound, for example, stannous chloride, stannous fluoride, stannous bromide, stannous iodide, or the like can be used.

[0035] (Silver coating step S03)

Next, the silver coating layer 12 is formed by electroless plating of silver on the surface of the resin particle 11.

Examples of a method of forming the silver coating layer 12 by electroless plating include: (1) a method in which the resin particle 11 is introduced into an aqueous solution containing a complexing agent, a reducing agent, and the like to prepare a slurry, and then an aqueous silver salt solution is added dropwise to the slurry; (2) a method in which the resin particle 11 is introduced into an aqueous silver salt solution containing a complexing agent to prepare a slurry, and then an aqueous reducing agent solution is added dropwise to the slurry; and (3) a method in which the resin particle 11 is introduced into an aqueous silver salt solution containing a complexing agent and a reducing agent to prepare a slurry, and then an aqueous caustic alkali solution is added dropwise to the slurry.

[0036] As the silver salt, silver nitrate, a material obtained by dissolving silver in nitric acid, or the like can be used. As the complexing agent, ammonia or salts such as ethylenediaminetetraacetic acid, tetrasodium ethylenediaminetetraacetate, nitrilotriacetic acid, triethylenetetraaminehexaacetic acid, sodium thiosulfate, a succinate, succinimide, a citrate, and an iodide salt can be used. As the reducing agent, formalin, glucose, imidazole, Rochelle salt (potassium sodium tartrate), hydrazine and derivatives thereof, hydroquinone, L-ascorbic acid, formic acid, or the like can be used. As the reducing agent, formaldehyde is preferable, a mixture of two or more reducing agents including at

least formaldehyde is more preferable, and a mixture of reducing agents including formaldehyde and glucose is most preferable.

[0037] When divalent tin ions are adsorbed on the surface of the resin particle 11 by the catalyzing treatment step S02, the divalent tin ions are converted into tetravalent ions and dissolve, thereby releasing divalent electrons. Then, silver ions receive the divalent electrons and are deposited as metallic silver. As a result, the silver coating layer 12 is efficiently formed.

However, when the contained amount of tin increases due to the catalyzing treatment step S02, the silver coating layer 12 may peel off from the resin particle 11 under a thermal cycle load. For this reason, it is necessary to consider how to carry out the catalyzing treatment step S02 in view of the contained amount of tin. In the present embodiment, since silicon oxide is provided on the surface of the resin particle 11, silver can be favorably plated on the surface of the resin particle 11 even when the catalyzing treatment step S02 is omitted.

Although the reason why the adhesion of silver is improved when the silicon oxide is formed on the surface is not clear, possible reasons include excellent affinity for deposited silver particles and an improved tin adsorption effect.

[0038] Through the steps as described above, the silver-coated resin particle 10 according to the present embodiment is produced.

[0039] The filler-containing paste according to the present embodiment contains a binder resin and the above-described silver-coated resin particle 10 as a filler. The filler-containing paste may contain a solvent and an additive as necessary.

The binder resin is not particularly limited, and examples thereof include a thermoplastic resin and a composition that cures by heat or light, such as a curable resin composition.

Examples of the thermoplastic resin include a styrene-butadiene block copolymer, an

acrylic resin, an ethylene-vinyl acetate resin, and a phenoxy resin. Examples of the thermosetting resin composition include a resin composition containing, as a main component, a resin such as a silicone resin and an epoxy resin, or a mixture thereof. In order to satisfy requirements for adhesion, hardness, electrical properties, electrothermal properties, and the like, a material having favorable compatibility with the silver-coated resin particles is suitable.

[0040] In order to improve affinity (compatibility) with the binder resin, the surface of the silver-coated resin particles may be subjected to a surface treatment with an organic acid or the like. Examples of the surface treatment include fatty acids such as stearic acid, isostearic acid, palmitic acid, and oleic acid; dicarboxylic acids such as maleic acid and succinic acid; carboxylic acid-based polymers such as polyacrylic acid; amine compounds such as dodecylamine and octadecylamine; amine-based polymers such as polyetheramine; sulfide compounds such as octadecyl disulfide; thiol compounds such as dodecanethiol; and silane coupling agents.

[0041] Further, in order to obtain higher electrical conductivity and thermal conductivity, a conductive filler other than the silver-coated resin particle 10 (hereinafter, referred to as an other conductive filler) may be added. Examples of the other conductive filler include metal particles such as silver powder, copper powder, and nickel powder, organic particles such as carbon, and conductive ceramic particles; and silver powder having excellent electrical conductivity and thermal conductivity is preferable. In addition, with regard to the particle shape, it is more preferable to use not only spherical particles but also flake-shaped (flat) particles. An addition proportion may be set to silver-coated resin particle 10:other conductive filler = 5% to 95% by mass:95% to 5% by mass, depending on the target electrical conductivity and thermal conductivity.

The filler-containing paste according to the present embodiment is produced by weighing

predetermined amounts of the binder resin (for example, the epoxy resin) and the above-described silver-coated resin particle 10, and kneading them by planetary stirring, a three-roll mill, or the like.

[0042] The filler-containing paste according to the present embodiment is used for forming a bonding layer 4 that bonds a circuit layer 2 of an insulated circuit board and a semiconductor element 3 in a semiconductor device 1, as shown in FIG. 3, for example. That is, by applying the filler-containing paste according to the present embodiment onto a mounting surface of the circuit layer 2, stacking the semiconductor element 3 thereon, and performing heating treatment, the bonding layer 4 formed of a cured product of the filler-containing paste according to the present embodiment is formed, and the circuit layer 2 and the semiconductor element 3 are bonded to each other.

[0043] Here, since the filler-containing paste according to the present embodiment contains the above-described silver-coated resin particle 10 as a filler, it is excellent in electrical conductivity and thermal conductivity, can electrically connect the semiconductor element 3 and the circuit layer 2, and can efficiently dissipate heat generated in the semiconductor element 3 to the insulated circuit board side. In addition, since the bonding layer 4 has excellent thermal cycle reliability, separation between the semiconductor element 3 and the circuit layer 2 can be suppressed even when a thermal cycle is applied.

[0044] With the silver-coated resin particle 10 according to the present embodiment configured as described above, since the silver-coated resin particle 10 contains silicon oxide in a range of 0.04% by mass or more and 3.00% by mass or less, silver can be favorably plated on the surface of the resin particle 11, and the amount of tin used in the catalyzing treatment step S02 can be reduced.

Since the contained amount of tin is limited to 0.20% by mass or less, peeling of the

silver coating layer 12 under a thermal cycle load can be suppressed.

[0045] In the present embodiment, when the 5% compression modulus (5% K value) of the silver-coated resin particle 10 is 2.5 GPa or less, the silver-coated resin particle 10 is sufficiently soft and easily deformed, so that, for example, the occurrence of cracks in a paste cured product of a filler-containing paste containing the silver-coated resin particle 10 as a filler can be suppressed.

[0046] In the present embodiment, when the resin composition constituting the resin particle 11 is one or more selected from an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin, the resin particle 11 has excellent flexibility and is particularly suitable as a filler.

[0047] In the present embodiment, when the particle diameter of the silver-coated resin particle 10 is in a range of 2 μm or more and 50 μm or less, the amount of expensive silver used can be reduced to lower costs, and the silver-coated resin particle 10 can be used as a filler for a paste or the like for forming a fine pattern.

[0048] With the filler-containing paste according to the present embodiment, since the filler-containing paste contains the silver-coated resin particle 10 according to the present embodiment as a filler, the filler-containing paste has excellent thermal cycle resistance and can be stably used as a conductive adhesive or a heat transfer material even in applications in which a severe thermal cycle is applied.

[0049] Although one embodiment of the present invention has been described above, the present invention is not limited thereto, and various modifications may be made without departing from the technical idea of the invention.

In the present embodiment, the filler-containing paste has been described as being applied to use in forming a bonding layer that bonds a circuit layer of a semiconductor device and a semiconductor element, but is not limited thereto and may be used for other

applications.

Examples

[0050] A confirmation experiment conducted to confirm the effectiveness of the present invention will be described.

[0051] (Inventive Examples 1 to 5 and Comparative Examples 2 and 3: wet method)

Resin particles having the materials and average particle diameters shown in Table 1 were dispersed in a solvent of water:ethanol = 1:1 to obtain a slurry having a concentration of solid contents of 5% by mass.

Methyl silicate (product name: MS-51, manufactured by Mitsubishi Chemical Corporation) was added to the slurry such that the silica concentration was the value shown in Table 1, and a very small amount of nitric acid was added dropwise thereto to produce silica-coated resin particles.

[0052] After performing filtration, washing, and drying treatment at 120°C for 5 hr, the particles were dispersed in water, stannous chloride was added thereto such that the tin concentration was the value shown in Table 1, and the mixture was stirred at 40°C for 1 hour and filtered again. The obtained cake was dispersed in water to obtain resin particles having divalent tin ions adsorbed on their surfaces (resin particles subjected to a catalyzing treatment).

Thereafter, a silver coating layer was formed on the surface of the resin particles by electroless plating such that the silver concentration was the value shown in Table 1.

[0053] (Inventive Examples 6 to 8 and Comparative Examples 4 to 6: dry method)

Resin particles having the materials and average particle diameters shown in Table 1 and silica nanoparticles having an average particle diameter of 50 nm were mixed such that the contained amount of the silica nanoparticles was the value shown in Table 1, and the mixture was treated using a planetary ball mill to attach the silica nanoparticles to the

surfaces of the resin particles.

A silver coating layer was formed on the resin particles having the silica nanoparticles attached to their surfaces by performing the catalyzing treatment and the electroless plating in the same manner as in Inventive Examples 1 to 5.

[0054] (Comparative Example 1)

Urethane particles (resin particles) having an average particle diameter of 15 μm were dispersed in water, stannous chloride was added thereto such that the tin concentration was 0.1% by mass, and the mixture was stirred at 40°C for 1 hour and filtered. The obtained cake was dispersed in water to obtain resin particles having divalent tin ions adsorbed on their surfaces (resin particles subjected to a catalyzing treatment).

A silver coating layer was formed on the surfaces of the resin particles by electroless plating such that the silver concentration was 45% by mass.

[0055] A 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Examples 1 to 8 and Comparative Examples 1 to 6 obtained as described above was calculated as follows. The evaluation results are shown in Table 1.

[0056] First, using a microcompression tester (manufactured by Fischer Instruments, model number: HM500), a compression test was carried out on one silver-coated resin particle with a flat indenter under conditions of a load change rate of 0.3 mN/s and 20°C, and the displacement and load when the silver-coated resin particle was compressed by 5% with respect to the major axis thereof were measured. At this time, a measurement starting point (zero point) of the displacement was not the point where the micro compression tester recognized contact with the silver-coated resin particle, but the point where the micro compression tester changed the load applied to the silver-coated resin particle. Next, the measured displacement and load were substituted into the following (1) to calculate the 5% compression modulus (5% K value).

[0057] Expression (1): 5% Compression modulus (5% K value) [GPa] = $3F/(2S^3R)^{1/2}$

F: Load when the silver-coated resin particle was compressed by 5% [N] S: Displacement when the silver-coated resin particle was compressed by 5% [mm] R: Radius of the silver-coated resin particle before compression [mm] [0058] In addition, after a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Examples 1 to 8 and Comparative Examples 1 to 6, cross sections thereof were observed by SEM to confirm the presence or absence of peeling. The evaluation results are shown in Table 1. Further, FIGS. 4A and 4B show the SEM observation results after the thermal cycle test of Inventive Example 1; FIG. 5 shows the SEM observation result after the thermal cycle test of Inventive Example 6; FIGS. 6A and 6B show the SEM observation results after the thermal cycle test of Comparative Example 5; and FIG. 7 shows the SEM observation result after the thermal cycle test of Comparative Example 6.

[0059] Furthermore, after a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Examples 1 to 8 and Comparative Examples 1 to 6, an epoxy resin-based filler-containing paste having a filler ratio of 60 vol% was prepared using a planetary centrifugal mixer. Using the filler-containing paste, a coating film having a thickness of 50 μm was formed.

A volume resistivity of the coating film was measured by a four-probe method in accordance with JIS-K-7194. The evaluation results are shown in Table 1.

[0060] [Table 1]

	Silver-coated resin particle						Evaluation		
	Resin particle		Providing method of silicon oxide	Contained amount of silicon oxide (% by mass)	Contained amount of tin (% by mass)	Coated amount of silver (% by mass)	5% Compression modulus (GPa)	Peeling after thermal cycling test	Volume resistivity of coating film (Ω·cm)
	Material	Particle diameter (μm)							

Inventive Example	1	Urethane	15	Wet	2.00	0.10	45	0.5	N	2.0×10^{-4}
	2	Urethane	6	Wet	0.05	0.12	65	1.9	N	1.0×10^{-4}
	3	Styrene	20	Wet	3.00	0.15	40	2.0	N	3.0×10^{-3}
	4	Urethane	50	Wet	1.00	0.10	24	0.4	N	1.0×10^{-3}
	5	Phenolic	10	Wet	0.30	0.20	50	2.5	N	5.0×10^{-4}
	6	Urethane	15	Dry	1.50	0.10	45	0.3	N	2.0×10^{-4}
	7	Acrylic	2	Dry	0.04	0.09	80	2.5	N	9.0×10^{-5}
	8	Acrylic	35	Dry	3.00	0.05	30	0.7	N	1.0×10^{-3}
Comparative Example	1	Urethane	15	None	0.00	0.10	45	0.5	Y	5.0×10^{-3}
	2	Styrene	10	Wet	0.04	0.35	50	2.6	Y	1.0×10^{-1}
	3	Phenolic	20	Wet	0.02	0.20	40	3.9	Y	3.0×10^{-2}
	4	Acrylic	50	Dry	3.10	0.00	24	2.0	Y	4.0×10^{-3}
	5	Urethane	15	Dry	1.50	0.35	45	2.8	Y	1.0×10^{-1}
	6	Urethane	6	Dry	7.20	0.40	65	5.0	Y	1.0×10^{-2}

[0061] In Comparative Example 1, peeling of the silver coating layer was confirmed after the thermal cycle test. It is presumed that this was because silicon oxide was not provided on the surfaces of the resin particles, and adhesion between the resin particles and the silver coating layer was insufficient. The 5% compression modulus (5% K value) was 0.5 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 1 was 5.0×10^{-3} Ω·cm.

[0062] In Comparative Example 2, peeling of the silver coating layer was confirmed after the thermal cycle test. It is presumed that this was because the contained amount of tin was as high as 0.35% by mass, and adhesion between the resin particles and the silver coating layer was insufficient. The 5% compression modulus (5% K value) was 2.6 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 2 was 1.0×10^{-1} Ω·cm.

[0063] In Comparative Example 3, peeling of the silver coating layer was confirmed after the thermal cycle test was carried out. It is presumed that this was because the contained amount of silicon oxide was as low as 0.02% by mass, and adhesion between the resin particles and the silver coating layer was insufficient. The 5% compression modulus (5% K value) was 3.9 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 3 was 3.0×10^{-2} Ω·cm.

[0064] In Comparative Example 4, peeling of the silver coating layer was confirmed after the thermal cycle test was carried out. It is presumed that this was because the contained amount of silicon oxide was as high as 3.1% by mass, and the flexibility of the resin particles decreased. The 5% compression modulus (5% K value) was 2.0 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 4 was 4.0×10^{-3} Ω·cm.

[0065] In Comparative Example 5, peeling of the silver coating layer was confirmed after the thermal cycle test. It is presumed that this was because the contained amount of tin was as high as 0.35% by mass, and adhesion between the resin particles and the silver coating layer was insufficient. The 5% compression modulus (5% K value) was 2.8 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 5 was 1.0×10^{-1} Ω·cm.

[0066] In Comparative Example 6, peeling of the silver coating layer was confirmed after the thermal cycle test. It is presumed that this was because the contained amount of tin was as high as 0.4% by mass, so that adhesion between the resin particles and the silver

coating layer was insufficient, and because the contained amount of silicon oxide was as high as 7.2% by mass, so that the flexibility of the resin particles decreased. The 5% compression modulus (5% K value) was 5.0 GPa.

Furthermore, the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 6 was 1.0×10^{-2} Ω·cm.

[0067] On the other hand, in Inventive Examples 1 to 8, silicon oxide was contained in a range of 0.04% by mass or more and 3.00% by mass or less, and the contained amount of tin was 0.20% by mass or less, and peeling of the silver coating layer was not confirmed after the thermal cycle test. It is presumed that this was because the contained amount of tin was low, and silicon oxide was contained in an appropriate amount, thereby sufficiently improving adhesion between the resin particles and the silver coating layer. In addition, it was confirmed that the volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Examples 1 to 8 was sufficiently low, and that a coating film having excellent electrical conductivity could be formed.

[0068] As described above, according to the present invention, it was found that it is possible to provide a silver-coated resin particle having excellent adhesion between the resin particle and the silver coating layer and having excellent thermal cycle resistance, and to provide a filler-containing paste containing the silver-coated resin particle as a filler.

INDUSTRIAL APPLICABILITY

[0069] The silver-coated resin particle and filler-containing paste of the present invention can be used as anisotropic conductive film-forming agents (ACF and ACP) used in liquid crystal displays, touch panels, and the like, conductive pastes used in touch panels and

the like, conductive pastes and films for die bonding, and thermal interface materials (TIM).

REFERENCE SIGNS LIST

[0070] 10 Silver-coated resin particle

11 Resin particle

12 Silver coating layer

CLAIMS

[Claim 1] A silver-coated resin particle comprising:

a resin particle formed of a resin composition; and

a silver coating layer formed on a surface of the resin particle,

wherein the silver-coated resin particle contains silicon oxide in a range of 0.04% by mass or more and 3.00% by mass or less, and a contained amount of tin is 0.20% by mass or less.

[Claim 2] The silver-coated resin particle according to Claim 1, wherein a 5% compression modulus (5% K value) is 2.5 GPa or less.

[Claim 3] The silver-coated resin particle according to Claim 1, wherein the resin composition is one or more selected from an acrylic resin, a styrene resin, a phenolic resin, a urethane resin, and a polyimide resin.

[Claim 4] The silver-coated resin particle according to Claim 1, wherein a particle diameter is in a range of 2 μm or more and 50 μm or less.

[Claim 5] A filler-containing paste comprising:

a binder resin; and

the silver-coated resin particle according to any one of Claims 1 to 4 as a filler.