DESCRIPTION

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

TECHNICAL FIELD

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

Priority is claimed on Japanese Patent Application No. 2024-061053, filed April 4, 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 Sn (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 silver-coated resin particles 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 particles 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 Sn 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 Sn. The present inventors have also found that, by

providing titanium 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 silver-coated resin particles according to an aspect 1 of the present invention are silver-coated resin particles each 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 particles contain titanium oxide in a range of 0.05% by mass or more and 12.00% by mass or less, and a contained amount of Sn is 0.20% by mass or less.

[0009] With the silver-coated resin particles according to the aspect 1 of the present invention, since titanium oxide is contained in a range of 0.05% by mass or more and 12.00% by mass or less, silver can be favorably plated on the surface of the resin particle, and the amount of Sn used in a catalyzing treatment can be reduced. In addition, since the contained amount of Sn is limited to 0.20% by mass or less, peeling of the silver coating layer under a thermal cycle load can be suppressed.

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

[0010] Silver-coated resin particles according to an aspect 2 of the present invention are characterized in that, in the silver-coated resin particles according to the aspect 1 of the present invention, a 5% compression modulus (5% K value) is in a range of 0.2 GPa or more and 3.5 GPa or less.

With the silver-coated resin particles according to the aspect 2 of the present invention, since the 5% compression modulus (5% K value) is in a range of 0.2 GPa or more and 3.5 GPa or less, the silver-coated resin particles maintain sufficient shape retention due to

the addition of filler and are sufficiently soft and easily deformable. Therefore, for example, occurrence of cracks in a paste cured product of a paste containing the silver-coated resin particles as a filler can be suppressed.

[0011] Silver-coated resin particles according to an aspect 3 of the present invention are characterized in that, in the silver-coated resin particles 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 particles 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 particles have excellent flexibility and are particularly suitable as a filler.

[0012] Silver-coated resin particles according to an aspect 4 of the present invention are characterized in that, in the silver-coated resin particles 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 particles 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 particles 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 particles according to any one of the aspects 1 to 3 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 particles 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 silver-coated resin particles having excellent adhesion between resin particles and a silver coating layer and having excellent thermal cycle resistance, and a filler-containing paste containing the silver-coated resin particles as a filler.

BRIEF DESCRIPTION OF DRAWINGS

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

[FIG. 2] A flowchart representing a method for producing silver-coated resin particles 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 silver-coated resin particles of Inventive Example 1 in Examples.

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

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

[FIG. 6A] A photograph showing a result of SEM observation of silver-coated resin particles of Comparative Example 2 in Examples.

[FIG. 6B] A photograph showing a result of SEM observation of silver-coated resin particles of Comparative Example 2 in Examples.

[FIG. 7] A photograph showing a result of SEM observation of silver-coated resin particles of Comparative Example 4 in Examples.

DESCRIPTION OF EMBODIMENTS

[0016] Hereinafter, silver-coated resin particles 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 silver-coated resin particles 10 according to an embodiment of the present invention. For example, the silver-coated resin particles 10 according to the present embodiment each include, 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 particles 10 contain titanium oxide in a range of 0.05% by mass or more and 12.00% by mass or less, and a contained amount of Sn is 0.20% by mass or less.

The silver-coated resin particles 10 may contain silicon oxide. A contained amount of silicon oxide is preferably 3.00% by mass or less.

[0018] Here, in the present embodiment, the contained amount of titanium oxide in the silver-coated resin particles 10 is calculated by collecting a measurement sample from the silver-coated resin particles 10, performing elemental analysis, and converting the measured Ti contained amount to a titanium oxide (TiO_2) equivalent.

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

[0019] In addition, in the silver-coated resin particles 10 according to the present embodiment, it is preferable that a 5% compression modulus (5% K value) is in a range of 0.2 GPa or more and 3.5 GPa or less.

In addition, in the silver-coated resin particles 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 particles 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 particles 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 particles 10 according to the present embodiment are defined as described above will be described below.

[0021] (Titanium oxide)

In the silver-coated resin particles 10 according to the present embodiment, by containing titanium oxide, 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. In addition, by incorporating a part of the titanium oxide in the resin particles, the strength of the particles is improved, and the particles can withstand mechanical deformation and high shear during dispersion.

Here, when the contained amount of titanium oxide in the silver-coated resin particles 10 is less than 0.05% by mass, there is a concern that adhesion between the resin particle 11 and the silver coating layer 12 cannot be sufficiently improved, and the hardness of the

silver-coated resin particles may be insufficient. On the other hand, when the contained amount of titanium oxide is more than 12.00% by mass, there is a concern that the flexibility of the silver-coated resin particles 10 may decrease.

For this reason, in the silver-coated resin particles 10 according to the present embodiment, the contained amount of titanium oxide is set in a range of 0.05% by mass or more and 12.00% 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 titanium oxide in the silver-coated resin particles 10 is preferably 1.50% by mass or more, and more preferably 3.00% by mass or more.

In addition, in order to further ensure the flexibility of the silver-coated resin particles 10, the contained amount of titanium oxide in the silver-coated resin particles 10 is preferably 10.00% by mass or less, more preferably 7.50% by mass or less, and still more preferably 5.00% by mass or less.

[0023] (Sn contained amount)

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

Therefore, in the silver-coated resin particles 10 according to the present embodiment, the contained amount of Sn 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 Sn in the silver-coated resin particles 10 is preferably 0.20% by mass or less, and more preferably 0.10% by mass or less.

In addition, the contained amount of Sn in the silver-coated resin particles 10 is not particularly limited, but in order to reliably improve the adhesion, the contained amount of Sn is preferably 0.00% by mass or more, and more preferably 0.05% by mass or more.

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

In the silver-coated resin particles 10 according to the present embodiment, when the 5% compression modulus (5% K value) is 3.5 GPa or less, the flexibility of the silver-coated resin particles 10 is sufficiently ensured, so that occurrence of cracks in a paste cured product of a paste containing the silver-coated resin particles 10 as a filler can be suppressed.

On the other hand, when the 5% compression modulus (5% K value) is 0.2 GPa or more, elasticity of the silver-coated resin particles 10 is ensured, and the shape retention of the paste and the coating film strength can be maintained.

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

In addition, in order to reliably maintain the shape retention of the paste and the coating film strength, the lower limit of the 5% compression modulus (5% K value) of the silver-coated resin particles 10 is more preferably 0.3 GPa or more.

[0027] (Particle diameter)

In the silver-coated resin particles 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 particles 10 according to the present embodiment, when the particle diameter is 50 μm or less, a paste containing the silver-coated resin particles 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 particles 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 particles 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 particles 10 according to the present embodiment will be described with reference to a flowchart of FIG. 2.

[0031] (Titanium oxide providing step S01)

First, titanium oxide is provided on the surface of the resin particle 11. Examples of a method of providing titanium oxide include a method of forming a titanate film on the surface of the resin particle 11 (production method 1), and a method of physically attaching titanium oxide particles to the surfaces of the resin particles 11 (production method 2). In addition, a trace amount of silicon oxide may be provided together with the titanium oxide.

[0032] As the production method 1, for example, the resin particle 11 is dispersed in a mixed solvent of water and ethanol, a predetermined amount of titanium isopropoxide is

added thereto, and a trace amount of water or the like is added thereto as a catalyst, whereby a titanate film can be formed on the surface of the resin particle 11.

As the production method 2, for example, the resin particle 11 and titanium oxide particles are mixed in predetermined amounts, and the mixture is subjected to a planetary ball mill or the like, whereby the titanium oxide particles can be attached to the surface of the resin particle 11. As the titanium oxide 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. In order to enhance adhesion to the resin particles and uniformity, titanium oxide particles surface-coated with an inorganic compound, an organic compound, a resin, or the like can also be used.

Furthermore, the titanium oxide can be added as particles or as an inorganic/organic titanium compound in a synthesis step (monomer polymerization step) of core resin particles, and can be included in the resin particles, not only on the surface. By causing the resin particles to contain the titanium oxide, deformation resistance of the silver-coated resin particles can be improved, and peeling of the silver film can be prevented.

[0033] (Catalyzing treatment step S02)

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

[0034] (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.

[0035] 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.

[0036] 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 Sn 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 Sn. In the present embodiment, since titanium 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 contained amount of Sn is reduced by the catalyzing treatment step S02.

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

[0037] Through the steps as described above, the silver-coated resin particles 10 according to the present embodiment are produced.

[0038] The filler-containing paste according to the present embodiment contains a binder resin and the above-described silver-coated resin particles 10 as a filler. 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.

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.

The filler-containing paste may contain a solvent and an additive as necessary.

Further, in order to obtain higher electrical conductivity and thermal conductivity, a conductive filler other than the silver-coated resin particles 10 (hereinafter, referred to as 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 particles 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 particles 10, and kneading them by planetary stirring, a three-roll mill, or the like.

[0039] 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.

[0040] Here, since the filler-containing paste according to the present embodiment contains the above-described silver-coated resin particles 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.

[0041] With the silver-coated resin particles 10 according to the present embodiment configured as described above, since the silver-coated resin particles 10 contain titanium oxide in a range of 0.05% by mass or more and 12.00% by mass or less, silver can be favorably plated on the surface of the resin particle 11, and the amount of Sn used in the catalyzing treatment step S02 can be reduced.

In addition, since the contained amount of Sn is limited to 0.20% by mass or less, peeling of the silver coating layer 12 under a thermal cycle load can be suppressed.

[0042] In the present embodiment, when the 5% compression modulus (5% K value) of the silver-coated resin particles 10 is in a range of 0.2 GPa or more and 3.5 GPa or less, the shape retention and mechanical strength of the silver coating film are maintained, and the silver-coated resin particles 10 are sufficiently soft and easily deformable. Therefore, for example, occurrence of cracks in a paste cured product of a filler-containing paste containing the silver-coated resin particles 10 as a filler can be suppressed.

[0043] 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.

[0044] In the present embodiment, when the particle diameter of the silver-coated resin particles 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 particles 10 can be used as a filler for a paste or the like for forming a fine pattern.

[0045] With the filler-containing paste according to the present embodiment, since the filler-containing paste contains the silver-coated resin particles 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.

[0046] 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

[0047] A confirmation experiment conducted to confirm the effectiveness of the present invention will be described.

[0048] (Inventive Examples 1 to 5 and Comparative Examples 2 and 3)

Resin particles shown in Table 1 were dispersed in an ethanol solvent to obtain a slurry having a concentration of solid contents of 5% by mass.

Titanium isopropoxide was added to the slurry such that the titanium oxide concentration

was the numerical value shown in Table 1, and a very small amount of water was added dropwise thereto to produce titania-coated urethane particles.

After filtration and washing, the particles were dispersed in water, stannous chloride was added thereto such that the tin concentration was the numerical value shown in Table 1, and the mixture was stirred at 40°C for 1 hr 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 Ag concentration was the numerical value shown in Table 1.

[0049] (Inventive Examples 6 to 8 and Comparative Examples 4 to 6)

Resin particles shown in Table 1 and titanium oxide particles having an average particle diameter of 200 nm were mixed such that the contained amount of the titanium oxide particles was the numerical value shown in Table 1, and the mixture was treated using a planetary ball mill to attach the titanium oxide particles to the surfaces of the resin particles.

A silver coating layer was formed by performing a catalyzing treatment and electroless plating on the resin particles having the titanium oxide particles attached to the surface thereof, in the same manner as in Inventive Examples 1 to 5 and Comparative Examples 2 and 3.

[0050] (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 Sn concentration was 0.1% by mass, and the mixture was stirred at 40°C for 1 hr 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 Ag concentration was 45% by mass.

[0051] The silver-coated resin particles of Inventive Examples 1 to 8 and Comparative Examples 1 to 6 obtained as described above were evaluated as follows.

[0052] (5% Compression modulus (5% K value) of silver-coated resin particles)

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 microcompression 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). The evaluation results are shown in Table 1.

[0053] 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] [0054] (Presence or absence of peeling of silver coating layer after thermal cycle load)

In addition, after a thermal cycle test between -20°C and 80°C was carried out on the obtained 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 of the silver coating layer. The evaluation results are shown in Table 1.

[0055] (Volume resistivity of coating film)

For the above-described silver-coated resin particles, an epoxy resin-based filler-containing paste having a filler ratio of 60 vol% was produced 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 (JIS-K-7194). The evaluation results are shown in Table 1.

[0056] [Table 1]

		Silver-coated resin particles						Evaluation		
		Resin particle		Providing method of titanium oxide	Contained amount of titanium 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	5.00	0.10	45	0.5	N	2.0×10^{-4}
	2	Urethane	6	Wet	3.50	0.12	65	1.9	N	1.0×10^{-4}
	3	Styrene	20	Wet	0.05	0.15	40	2.0	N	9.0×10^{-5}
	4	Urethane	50	Wet	0.33	0.10	24	0.4	N	1.0×10^{-3}
	5	Phenolic	10	Wet	1.50	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	2.70	0.09	80	2.5	N	3.0×10^{-3}
	8	Acrylic	35	Dry	12.00	0.05	30	0.7	N	1.0×10^{-3}
Comparative Example	1	Urethane	15	None	0.00	0.10	45	0.5	Y	2.0×10^{-3}
	2	Styrene	10	Wet	0.10	0.35	50	2.6	Y	1.0×10^{-1}
	3	Phenolic	20	Wet	0.00	0.20	40	3.9	Y	3.0×10^{-2}
	4	Acrylic	50	Dry	7.50	0.00	24	2.0	Y	4.0×10^{-3}
	5	Urethane	15	Dry	5.00	0.35	45	2.8	Y	1.0×10^{-1}
	6	Urethane	6	Dry	15.00	0.40	65	5.0	Y	1.0×10^{-2}

[0057] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 1 was 0.5 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 1, cross sections thereof were observed by SEM. The observation results are shown in FIGS. 4A and 4B. Even after the thermal cycle test, peeling of the silver coating layer was not observed.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 1 as a filler was 2.0×10^{-4} Ω·cm.

[0058] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 2 was 1.9 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 2, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed. The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 2 as a filler was 1.0×10^{-4} Ω·cm.

[0059] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 3 was 2.0 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 3, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed. The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 3 as a filler was 9.0×10^{-5} Ω·cm.

[0060] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 4 was 0.4 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 4, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed. The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 4 as a filler was 1.0×10^{-3} Ω·cm.

[0061] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 5 was 2.5 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 5, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed. The volume resistivity of the coating film formed of the filler-containing paste containing

the silver-coated resin particles of Inventive Example 5 as a filler was 5.0×10^{-4} Ω·cm.

[0062] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 6 was 0.3 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 6, cross sections thereof were observed by SEM. The observation results are shown in FIG. 5. Even after the thermal cycle test, peeling of the silver coating layer was not observed.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 6 as a filler was 2.0×10^{-4} Ω·cm.

[0063] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 7 was 2.5 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 7, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 7 as a filler was 3.0×10^{-3} Ω·cm.

[0064] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 8 was 0.7 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 8, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 8 as a filler was 1.0×10^{-3} Ω·cm.

[0065] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Inventive Example 8 was 0.7 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Inventive Example 8, cross sections thereof were observed by SEM. Even after the thermal cycle test, peeling of the silver coating layer was not observed.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Inventive Example 8 as a filler was 1.0×10^{-3} Ω·cm.

[0066] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 1 was 0.5 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Comparative Example 1, cross sections thereof were observed by SEM. Peeling of the silver coating layer was confirmed after the thermal cycle test.

The volume resistivity of the coating film formed of the filler-containing paste containing the silver-coated resin particles of Comparative Example 1 as a filler was 2.0×10^{-3} Ω·cm.

[0067] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 2 was 2.6 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Comparative Example 2, cross sections thereof were observed by SEM. The observation results are shown in FIGS. 6A and 6B. Peeling of the silver coating layer was confirmed after the thermal cycle test.

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

[0068] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 3 was 3.9 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated

resin particles of Comparative Example 3, cross sections thereof were observed by SEM. Peeling of the silver coating layer was confirmed after the thermal cycle test.

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

[0069] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 4 was 2.0 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Comparative Example 4, cross sections thereof were observed by SEM. The observation results are shown in FIG. 7. Peeling of the silver coating layer was confirmed after the thermal cycle test.

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

[0070] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 5 was 2.8 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated resin particles of Comparative Example 5, cross sections thereof were observed by SEM. Peeling of the silver coating layer was confirmed after the thermal cycle test.

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

[0071] The measured 5% compression modulus (5% K value) of the silver-coated resin particles of Comparative Example 6 was 5.0 GPa.

After a thermal cycle test between -20°C and 80°C was carried out on the silver-coated

resin particles of Comparative Example 6, cross sections thereof were observed by SEM. Peeling of the silver coating layer was confirmed after the thermal cycle test.

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

[0072] As described above, according to the present invention, it was found that it is possible to provide silver-coated resin particles having excellent adhesion between the resin particles and the silver coating layer and having excellent thermal cycle resistance, and to provide a filler-containing paste containing the silver-coated resin particles as a filler.

INDUSTRIAL APPLICABILITY

[0073] The silver-coated resin particles 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

[0074] 10 Silver-coated resin particle

11 Resin particle

12 Silver coating layer

CLAIMS

[Claim 1] Silver-coated resin particles each 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 particles contain titanium oxide in a range of 0.05% by mass or more and 12.00% by mass or less, and a contained amount of Sn is 0.20% by mass or less.

[Claim 2] The silver-coated resin particles according to Claim 1, wherein a 5% compression modulus (5% K value) is in a range of 0.2 GPa or more and 3.5 GPa or less.

[Claim 3] The silver-coated resin particles 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 particles 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 particles according to any one of Claims 1 to 4 as a filler.