

TITLE OF THE INVENTION
CONDUCTIVE PASTE COMPOSITIONS FOR
CHIP RESISTOR TERMINAL ELECTRODES ✓

FIELD OF THE INVENTION

The present invention relates to electrically conductive pastes, composed of electrically conductive ingredients and inorganic binders dispersed in an organic binder, which can be used as the terminal electrode material in chip components. It relates in particular to electrically conductive pastes which, even when noble metals are used as the electrically conductive ingredients, have a good solder leach resistance during the mounting of chip components onto a circuit substrate and are highly suitable as compositions for chip resistor electrodes.

BACKGROUND OF THE INVENTION

With the trend toward the higher-density packaging of electronic circuits, chip mounting whereby a plurality of miniaturized circuit components (referred to here as "chip components"), i.e., chip resistors and chip capacitors, are mounted onto a circuit substrate at the same time has come to be widely used in the past few years.

Lead-out terminal electrodes for packaging on the circuit substrate are invariably provided on these chip components.

The thick-film conductor paste compositions that have hitherto been widely used as these terminal electrode materials contain as the principal ingredients electrically conductive ingredients, binders and organic vehicles. Finely divided powders of the noble metals palladium (Pd), platinum (Pt) and silver (Ag), or mixtures or alloys thereof, or the oxides of palladium and silver, or mixtures thereof, are widely used as the conductive ingredients. Glass binders are used as the binders, and inert organic liquids are used as the organic vehicles. A paste-like composition having a suitable consistency and rheology is prepared by mixing the conductive ingredients, glass binders and inert organic vehicles, then carrying out dispersion by means of mechanical mixing.

The attachment of chip components such as these onto the surface of a circuit substrate pattern is generally accomplished by means of soldering, with the sustained fixing of the chip component terminals to the land area where they are positioned in the circuit pattern on the copper-clad laminated board for a printed circuit being carried out with molten solder.

Therefore, this conductive paste composition must not only have bond strength and electrical conductivity after formation of the terminal electrode, it must also be solderable. The solderability of this terminal electrode refers to the good solder wettability and solder leach resistance required for solder treatment of the terminal electrode during the mounting of chip components onto a circuit substrate or during repairs.

The inventors investigated the above-described prior art, as a result of which they learned of the following problems.

It is practically advantageous to use, as the conductive ingredient in the conductive paste compositions which serve as the terminal electrode material for these chip components, a silver-based conductor ingredient that has a low electrical connection resistance and a good solder wettability, and that can be oxidation fired. However, in cases where the terminal electrode has been formed with a conductive paste composition containing a silver-based conductor ingredient, one problem has been the poor solder leach resistance. Moreover, when RuO₂-based or pyrochlore-based chip resistor terminal electrodes are formed, other problems arise after electrode formation, such as fluctuations in the resistance value.

The first of the above-described problems is the phenomenon whereby, when a prior-art conductive paste composition is used as the chip component terminal electrodes and soldering is carried out directly on the electrodes, the silver serving as the principal conductor ingredient in the terminal electrode diffuses within the solder (this is known as solder leaching), and the tin serving as an ingredient of the solder diffuses within the conductor. When the solder leaching of electrodes arise during the mounting of components, this results in a decrease in reliability due to poor connection. When the solder leaching of electrodes arises during component repair, there is virtually no solder wetting of the electrodes, making it impossible to mount the components. The diffusion of tin into the electrode destroys the adhesion at the interface between the electrode and the chip body. A method for avoiding this consists of inhibiting the diffusion of silver into the solder by using an alloy of silver and palladium as the electrode conductor. However, even in cases such as this, solder leaching cannot be prevented when the solder temperature is high, and depending on the type of solder. Hence, the conditions of use are limited.

A second problem is that, in the production process for chip resistors and the like, when the chip resistor terminal electrode is formed by firing using a conductor paste composition, interdiffusion and thermal stress arise between the resistor and the terminal electrode, which causes a major fluctuation in the resistance values of the resistor.

According to one object of this invention, there are provided conductor paste compositions which, even though they use silver-based conductor ingredients, have an adequate conductivity and bonding strength, as well as a good balance in the overall properties, including solder wettability and resistance to solder leaching, and can form chip resistor terminal electrodes.

According to another object of the invention, there are provided conductor paste compositions for chip resistor terminal electrodes, which compositions contain, as the conductive inorganic fillers, metal oxides and/or pyrochlores and/or borites that do not diffuse within the solder during soldering and inorganic glass binder having a good resistance to plating solution and are composed of a silver-based conductor ingredient.

The above and other objects of the invention, as well as its novel features, shall become apparent from the description given in this specification and from the attached diagram.

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DETAILED DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the measurement circuit used to evaluate the electrical conductivity due to solder leaching after printing, drying and firing of the conductor paste composition.

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DETAILED DESCRIPTION OF THE INVENTION

The present invention, which was conceived in order to resolve the above problems, is a conductor paste composition for chip resistor terminal electrodes whereby, in an electrically conductive paste composition for chip resistor terminal electrodes that includes a metal powder as the electrically conductive ingredient, inorganic binders, and a vehicle: the metal powder serving as the electrically
15 conductive ingredient includes silver powder, palladium powder, a silver-palladium alloy powder, or a powder mixture of at least two of these, the inorganic binders include a glass binder and a conductive inorganic filler includes binary oxides and/or pyrochlores and/or borides of metals selected from the group consisting of iridium, rhodium, ruthenium, rhenium and tin.

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In the conductor paste compositions of the present invention, even when the silver-based conductive ingredient is leached by solder after terminal electrode formation, at least one conductive inorganic filler from among the binary metal oxides and pyrochlores and borides remains within the thick-film conductor that
25 forms the terminal electrode. As a result, sufficient conductivity and adhesive strength are maintained, in addition to which this makes it possible to prevent both a decline in reliability due to connection failure on account of solder leaching, and the inability to mount chip components because of a deterioration in the solder wettability.

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It is possible to use as the electrically conductive powder employed in this invention at least silver, palladium, and mixtures or alloys thereof, that have a low electrical connection resistance, a good solder wettability, and can be oxidation fired. Mixtures of these with other noble metal powders can also be used. These metals or alloys are used in the form of a finely divided powder. The particle size
35 of the metal powder is not particularly important, so long as it is suitable for the coating method, although it is preferable that this fall within a range of about 0.1-5 microns.

With regard to the glass binder used in this invention, the composition of the glass is not in itself critical. Anything may be used that does not react with the conductor phase described above, and that has a sufficient viscosity and glass fluidity at the firing temperature to assist in the sintering of the metal particles that
40 form the conductor phase in the firing step.



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5 Hence, it is possible to use a broad range of oxide glasses containing conventional glass-forming and glass-modifying ingredients. Examples of these oxide glasses include lead silicates such as lead borosilicate and lead silicate proper. The preferred glass is PbO-SiO_2 based glass frits or $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$ based glass frits, which has softening temperature of about $450\text{-}600^\circ\text{C}$ and resistance to plating solution. Such glasses do not comprise Bi_2O_3 as glass components composing the glasses because of poor resistance to plating solution.

10 There are no particular critical values for the particle size of the glass binder. However, the glass particles should be within a range of 0.1-10 microns (and preferably 0.5-5 microns), and the average particle size should be 2-3 microns. Finely divided glass smaller than 0.1 micron has a very large surface area, and requires a large amount of organic solvent to obtain a suitable fluidity as a printing paste. On the other hand, when the particles are larger than 10 microns
15 in size, this serves as a hindrance to printing.

The amount of silver in the composition will usually be 50-87 wt% on a paste basis, the amount of glass frit in the composition will ordinarily be from 3 to 10 wt% of the composition, and the amount of conductive inorganic filler will ordinarily be from 0.1-15 wt%, basis paste.

20 In this invention, the above-described conductive powder and glass binder, as well as the other inorganic fillers, can be dispersed in an organic vehicle and thereby prepared as a dispersion called a "paste" that generally has a semifluid softness.

25 The ratio, in the thick-film paste compositions of the present invention, of the organic vehicle to the inorganic solids in the dispersion depends upon the paste application method and the organic solvent used, and can be varied.

In order to obtain a good coating, the dispersion generally contains 50-90% by weight of inorganic solids and 10-50% by weight of vehicle.

30 Any inert liquid may be used as the vehicle. Water or any of various organic liquids to which thickening agents and/or stabilizers and/or other common additives have or have not been added can be used as the vehicle. Examples of organic liquids which can be used include aliphatic alcohols; the esters of such alcohols, such as the acetate and propionate esters; terpenes, such as turpentine and terpineol; as well as solutions of resins such as a lower alcohol
35 polymethacrylate, or solutions of ethyl cellosolve, in a solvent such as turpentine and the monobutyl ether of ethylene glycol monoacetate. A volatile liquid can be included in the vehicle so as to promote rapid hardening following application to the substrate, or the vehicle itself may be composed of this.

40 Preferable vehicles are those in which ethyl cellosolve and β -terpineol serve as the base.

Modes for carrying out the invention are described below, although the invention is not restricted by these examples. Unless noted otherwise, the numbers indicating the ingredient proportions represent parts by weight.

45 The glass used as the inorganic binder in the examples of the invention and comparative examples presented below was a $\text{PbO-SiO}_2\text{-B}_2\text{O}_3$ -based glass frit.

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EXAMPLES

Examples 1-12

A conductor paste composition was prepared by working together silver powder (finely ground to a particle size no greater than 1 μm), palladium powder, glass powder, ethyl cellulose and terpineol into the form of a paste, mixing this with a mixer, then mill-processing. The proportions of the individual ingredients were as follows.

TABLE 1

Examples of the Invention

Ingredient	1	2	3	4	5	6	7	8	9	10	11	12
Ag powder	68	68	68	68	68	68	68	68	56	56	65	63
Pd powder	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Glass powder	10	8	6	10	8	6.7	8.3	8	10	10	10	10
Inorganic Filler:												
Ruthenium oxide				1.5	1.5			0.75				
Bismuth pyrochlore	3.5	3.5	3.5			2.18	2.82	1.75				
Nickel boride (Ni_3B)									10			
Lanthanum boride (LaB_6)										10		
Tin oxide (SnO_2)											2.0	4.0
Resin:												
Ethyl cellulose	2	2	2	2	2	2	2	2	2	2	2.0	2.0
Organic Solvent:												
Terpineol	16	18	20	18	20	20.62	18.38	19	21.5	21.5	20.5	20.5

Comparative Examples

The conductor paste compositions in Comparative Examples 1-3 were prepared from the following ingredients by the same method as in Application Example 1.

TABLE 2

Comparative Examples

	1	2	3
Ag powder	68	71.5	68
Pd powder	2	0.5	2
Glass powder	5	3	5
Resin (ethyl cellulose)	2	2	2
Organic solvent (terpineol)	23	23	23

In the conductor paste compositions of these examples and the comparative examples, the electrical conductivity due to solder leaching at the time of soldering was evaluated (presence/absence of electrical connection failure) by the following method.

Next, the conductor paste compositions in the application examples and the comparative examples were printed in the pattern 2 shown in Fig. 1 using a 96% alumina substrate, this being done in the measurement circuit shown in Fig. 1 for evaluating the relationship between solder leaching and electrical conductivity after printing, drying and firing of the conductor paste composition,

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following which it was dried for 10 minutes at 150°C so as to give a thick film of 20-24 microns, then fired in an oxidizing atmosphere within an ordinary electrical belt furnace at 850°C and for a holding time of 10 minutes, such that the total firing time became about 30 minutes.

- 5 The resistance values for the thick-film conductors that were formed on the substrate when the conductor paste compositions of the application examples and comparative examples that had been fired in this way were dipped for 5, 10, 15 and 20 seconds into a molten eutectic solder (Sn:Pb = 63.37) maintained at about 280°C were measured using a commonly used four-terminal method for measuring resistance. Measurement was carried out, as shown in Fig. 1, using a resistance measuring device (e.g., an Advantest R6871 digital multimeter) that was electrically connected to the thick-film conductor pattern 2 formed on the substrate. The results are given in Table 3 below. From Table 3, it is apparent that conductor paste compositions according to this invention which use a silver-based conductor ingredient, and which are moreover pastes that contain a conductive inorganic filler, suppress electrical connection failure due to solder leaching. Moreover, it was also confirmed that all the other basic performance properties required of conductor paste compositions such as this (e.g., electrical conductivity, adhesion, etc.) are all at least of a degree that poses no practical problems.

TABLE 3

Solder Dipping Time

	5 seconds (Ω)	10 seconds (Ω)	15 seconds (Ω)	20 seconds (Ω)
Application Example 1	1.2	1.2	1.2	1.2
Application Example 2	1.1	1.1	1.1	1.0
Application Example 3	1.0	1.0	1.0	1.0
Application Example 4	1.0	1.0	1.0	1.0
Application Example 5	1.0	1.0	1.0	1.0
Application Example 6	1.0	1.0	1.0	1.0
Application Example 7	1.0	1.1	1.0	1.0
Application Example 8	1.0	1.0	1.0	1.0
Application Example 9	6.8	7.0	7.1	7.6
Application Example 10	1.5	1.5	1.6	1.7
Application Example 11	1.5	1.8	1.8	1.9
Application Example 12	1.8	2.0	2.1	2.3
Comparative Example 1	0.5	Not measurable	Not measurable	Not measurable
Comparative Example 2	0.5	Not measurable	Not measurable	Not measurable
Comparative Example 3	0.5	Not measurable	Not measurable	Not measurable

- 25 The primary advantageous effects achieved by this invention may be briefly summarized as follows.

By additionally including as inorganic fillers the binary oxides and/or pyrochlores and/or borides of metals selected from the group consisting of tin, iridium, rhodium, ruthenium and rhenium in an electrically conductive paste composition for chip resistor terminal electrodes containing a metal powder as the conductive ingredient, an inert binder and a vehicle, it was possible to maintain an

- 5 electrical connection even when the conductive ingredient has been leached by solder. Moreover, conductor paste compositions were obtained in which the electrical conductivity as well as the adhesive strength were adequate, and all the properties, including solder wettability and solder leach resistance, exist in a good balance.

CLAIMS

5 What is claimed is:

1. A conductor paste composition for chip resistor terminal electrodes comprising finely divided particles of (a) 50-87 wt% metallic silver, its alloy or mixtures thereof; (b) 3-10 wt% inorganic binder consisting of a glass frit essentially consisting of PbO , SiO_2 and optionally B_2O_3 without Bi_2O_3 , and (c) 0.1-15 wt% at least one selected from a group consisting of tin oxides, iridium oxides, rhodium oxides, ruthenium oxides, rhenium oxides, iridium-based, rhodium-based and ruthenium-based pyrochlores and borides, basis paste, all of (a), (b) and (c) being dispersed in (d) an organic medium.
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