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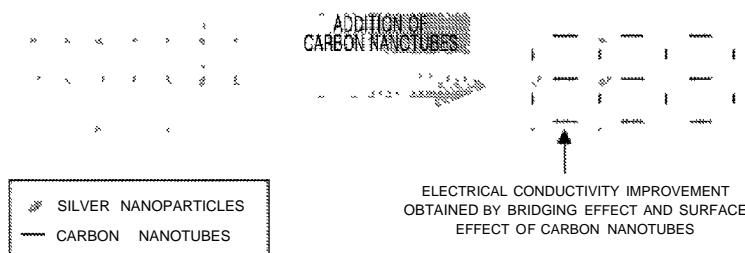
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(54) Title: CONDUCTIVE PASTE AND CONDUCTIVE CIRCUIT BOARD PRODUCED THEREWITH

[Fig. 1]



(57) Abstract: Disclosed is a conductive paste that has a high level of electrical conductivity with a small amount of silver and is suitable for forming a circuit wire. The conductive paste comprises 15 to 50 weight % of silver nanoparticles and 0.1 to 2.5 weight % of carbon nanotubes. Provided is also a conductive paste comprising 1 to 10 weight % of silver nanoparticles, 30 to 60 weight % of silver microparticles and 0.1 to 1 weight % of carbon nanotubes. The conductive pastes can be sintered at a low temperature of 150 °C or less.

Description

Title of Invention: CONDUCTIVE PASTE AND CONDUCTIVE CIRCUIT BOARD PRODUCED THEREWITH

Technical Field

- [1] The present invention relates to a conductive paste or ink containing silver nanoparticles. And, the present invention relates to a conductive circuit board having a circuit wire formed using the paste or ink.

Background Art

- [2] Information communication devices such as liquid crystal display and so on move toward miniaturization and high performance, and attempts have been steadily made to incorporate these devices on flexible material supports. The circuit wire of said devices is generally formed by forming a film by vapor deposition such as chemical vapor deposition (CVD), sputtering and so on, and etching out an unnecessary portion by photolithography and so on.
- [3] However, the conventional method for forming a circuit wire has disadvantages caused by repetition of film formation and etching, for example, a low usage efficiency of raw materials, generation of a large amount of waste, a long manufacturing time and a considerable installation cost. And, the conventional method encounters with many problems in forming a fine circuit wire required for miniaturization of said devices.
- [4] To solve the problems, recently the related industries pay attention to an ink-jet printing or a roll printing. These printing techniques allow a low loss of raw materials, non-use of hazardous components such as lead or the like, and a simple process for forming a circuit wire. More than anything else, said techniques support formation of a thinner and finer circuit wire than the conventional techniques. However, to form a circuit wire by said techniques, development of a high-performance conductive paste or ink is needed.
- [5] A conductive ink suitable for forming a circuit wire should have a specific resistivity of $1 \times 10^{-5} \Omega\text{-cm}$ or less for a high conductivity. However, it is not preferable to use a costly conductive filler so as to achieve said specific resistivity.
- [6] And, when printing the conductive paste on a flexible circuit board material such as polyethylene terephthalate (PET) and so on, one of the most important things is a sufficiently low sintering temperature because plastics or the like have a low glass transition temperature (T_g). The sintering temperature is set depending on the characteristics of a conductive filler (generally metal particles) and other components of the conductive paste. However, as the smaller metal particles have higher surface energy, the sintering temperature tends to be even lower than an intrinsic melting point of a

metal.

- [7] Silver has a high conductivity, and thus is suitable as a conductive filler of a conductive paste for forming a fine circuit wire. However, the use of a large amount of silver increases cost. And, silver has a poor adhesion with a widely utilized circuit board material and a difficulty in forming a smooth circuit wire. Furthermore, silver cannot achieve both a low sintering temperature and a low cost at the same time. It is preferred to use silver having a particle size of nanometer or smaller level so as to lower the sintering temperature of the conductive paste. However, in this case, it requires more cost than the use of silver having a particle size of micrometer or larger level. Conventionally, silver was used at an amount of 50 weight% or more or 80 weight% or more to the maximum based on the weight of the conductive paste so as to attain a desired level of conductivity of the conductive paste. If the content of silver does not come up to the range, the gap creates between silver particles, so that the silver particles are not electrically connected. Although there are electrical contacts between silver particles, the number of electrical contacts is very small, causing insufficient conductivity. In the case of screen printing, it is easy to control the viscosity of the conductive paste having a high content of silver to a suitable level for spray through a mesh net. However, a high content of silver nanoparticles having a high tendency to agglomerate increases cost, and needs an additive such as a dispersant, a stabilizer or the like, to ensure storage stability of the conductive paste. Because the additive generally has a high molecular weight of 10,000 or more, the use of the additive increases the sintering temperature again. That is, the sintering temperature reduction effect obtained by reducing the particle size of silver comes to nothing due to the increased silver content for a high conductivity.

- [8] For these reasons, the conventional conductive paste containing silver uses a high concentration of silver to form a continuous electrical network, thereby lowering a specific resistivity down to $1 \times 10^{-5} \Omega\text{-cm}$ or less. And, when the particle size of silver is 20 nm or smaller (level of silver nanoparticles), the conventional conductive paste has a minimum limit of sintering temperature of about 150°C . In summary, the conventional conductive paste has the limited particle size of silver to achieve a low sintering temperature and a high electrical conductivity. And, a large amount of silver having a particle size of a predetermined level or smaller causes side effects of a cost rise and a high sintering temperature resulted from the use of an additive such as a stabilizer. Under these circumstances, there is still a demand for a conductive paste that solves the problems and has a good adhesion with a circuit board material and a suitable viscosity for printing.

Disclosure of Invention

Technical Problem

- [9] Therefore, it is an object of the present invention to provide a conductive paste containing silver that has relatively less restrictive requirements in the particle size of silver, a lower sintering temperature than conventional pastes, and a high electrical conductivity with a low silver content.

Solution to Problem

- [10] To achieve the object, the present invention provides a conductive paste that contains silver nanoparticles, carbon nanotubes, a binder and a solvent, and can be sintered at a temperature of 150 °C or lower. According to an aspect of the present invention, the conductive paste comprises 15 to 50 weight% of silver nanoparticles having an average particle size of 1 to 100 nm based on the total weight of the conductive paste; 0.1 to 2.5 weight% of carbon nanotubes having an average diameter of 2 to 40 nm based on the total weight of the conductive paste; and 1 to 15 weight% of a binder based on the total weight of the conductive paste. The conductive paste may further comprise a solvent, or a solvent and an additive.
- [11] According to another aspect of the present invention, a conductive paste is provided that contains silver microparticles and can be sintered at a temperature of 150 °C or lower. The conductive paste comprises 1 to 10 weight% of silver nanoparticles having an average particle size of 1 to 100 nm based on the total weight of the conductive paste; 30 to 60 weight% of silver microparticles having an average particle size larger than 0.1 μm and not exceeding 50 μm , based on the total weight of the conductive paste; 0.1 to 1 weight% of carbon nanotubes having an average diameter of 2 to 40 nm based on the total weight of the conductive paste; 1 to 15 weight% of a binder based on the total weight of the conductive paste; and a solvent, or a solvent and an additive.
- [12] In the conductive paste of the present invention, the carbon nanotubes have an average length of 5 to 50 μm . And, the conductive paste has a specific resistivity of 2×10^6 to $10 \times 10^{-6} \Omega\text{-cm}$.
- [13] Furthermore, the present invention provides a conductive circuit board having a circuit wire formed using the conductive paste.

Advantageous Effects of Invention

- [14] According to the present invention, the conductive paste containing silver has relatively less restrictive requirements in the particle size of silver. That is, the conductive paste of the present invention may contain silver microparticles in addition to silver nanoparticles. The conductive paste can be sintered at a temperature of 150 °C or lower, resulting in good processability. And, the conductive paste contains carbon nanotubes, and thus remarkably reduces a usage amount of silver, compared with conventional pastes, resulting in improved economical efficiency while achieving a high

electrical conductivity. With the carbon nanotubes, the conductive paste has an improvement in adhesion with a circuit board material and is easy to control its viscosity to a suitable level for printing, due to a bridging effect as a filler. For screen printing, the conductive paste should have viscosity and thixotropy of a certain level or higher. The carbon nanotubes can provide said characteristics to the conductive paste with a small amount.

- [15] The conductive paste of the present invention can be widely used to form a circuit wire by printing. For example, the conductive paste can be used to form circuit wires for printed circuit boards and display devices such as a liquid crystal display, a plasma display panel, an organic light-emitting diode and so on, to manufacture an antenna for a radio-frequency identification (RFID) system, to produce an electrode for a solar cell, and to form a reflective film for a solar cell and so on.

Brief Description of Drawings

- [16] FIG. 1 is a view illustrating the principle of the present invention that carbon nanotubes electrically connect silver nanoparticles serving as a sole conductor in a conductive paste to significantly improve an electrical conductivity.
- [17] FIG. 2 is a graph illustrating the relationship between the content of carbon nanotubes and electric conductivity and indicating a percolation point of a conductive paste containing solely carbon nanotubes.
- [18] FIG. 3 is an SEM cross-sectional image of a circuit electrode formed according to example 2, in which an electrical network having carbon nanotubes distributed between silver nanoparticles is formed.
- [19] FIG. 4 is an SEM surface image of a circuit electrode formed according to example 2, in which metallization is accomplished after sintering.

Best Mode for Carrying out the Invention

- [20] Hereinafter, the present invention will be described in detail. The present invention provides a conductive paste containing carbon nanotubes. The conductive paste has a high electrical conductivity and a low sintering temperature with a smaller content of silver nanoparticles than the conventional paste.
- [21] According to an aspect of the present invention, the conductive paste comprises 15 to 50 weight% of silver nanoparticles having an average particles size of 1 to 100 nm, 0.1 to 2.5 weight% of carbon nanotubes having an average diameter of 2 to 40 nm, 1 to 15 weight% of a binder, based on the total weight of the conductive paste, and a solvent. The conductive paste may further comprise an additive. The conductive paste of the present invention can be sintered at a low temperature of 150 °C or less.
- [22] Preferably, the silver nanoparticles of the present invention has an average particle size of 1 to 100 nm. If the average particle size of the silver nanoparticles is smaller

than 1 nm, the conductive paste has a very low viscosity, which makes it difficult to form a circuit board having a certain thickness or larger. However, the present invention does not need to use silver nanoparticles having an average particle size of 20 nm or less for a high conductivity and a low sintering temperature, as was the case for the prior art. And, the silver nanoparticles are not limited to specific shape. The silver nanoparticles may have a shape of, for example, sphere, flake and so on. One of advantages of the present invention is to attain both a low sintering temperature and a high electrical conductivity at the same time due to configuration containing carbon nanotubes. The larger silver nanoparticles are, the better effects in aspects of cost and storage stability. Thus, the silver nanoparticles preferably have an average diameter larger than 20 nm and not exceeding 100 nm. The silver nanoparticles used in the conductive paste of the present invention may be used without coating or surface modification, or surface-modified for hydrophilic or hydrophobic property or surface-coated with a coating material such as a protective colloid forming material and so on.

[23] Preferably, the silver nanoparticles are included at an amount of 15 to 50 weight% based on the total weight of the conductive paste. This content is even lower than that of conventional pastes, and thus results in both a high electrical conductivity and cost reduction. If the content of silver nanoparticles is less than 15 weight%, the conductive paste has a poor electrical contact between silver nanoparticles, resulting in a large resistivity. If the content of silver nanoparticles is more than 50 weight%, improvement in conductivity to cost rise is insignificant.

[24] In the conductive paste of the present invention, the carbon nanotubes establish an electrical connection between the silver particles or are attached to the surface of the silver particles to substantially increase the surface area of the silver particles. Accordingly, the carbon nanotubes reduce the silver content required to achieve the same level of conductivity due to their bridging effect. And, the carbon nanotubes of the present invention allows use of silver nanoparticles having a particle size of 20 nm or more without a sacrifice of sintering temperature of the conductive paste. Furthermore, the carbon nanotubes improves adhesion with a circuit board material and facilitates to control the viscosity of the conductive paste to a suitable level for printing. These advantages are naturally obtained by the reduced amount of an inorganic substance as a filler occupying the conductive paste. In particular, the typical carbon nanotubes has some extent of surface defects in a graphene sheet. Thus, a functional group, such as a carboxyl group and so on, protrudes from the surface of the defects in the manufacture. Because the carbon nanotubes contain the functional group, it is possible to increase the adhesion of the conductive paste to the surface of the circuit board, which is not intended to be tied to a specific theory.

[25] In the present invention, the content of the carbon nanotubes is selected in con-

sideration of a target electrical conductivity, the content of silver nanoparticles and so on. The inventors studied the relationship between electrical conductivity and the content of carbon nanotubes to set a proper content of carbon nanotubes in the conductive paste. A conductive paste containing solely multiwalled carbon nanotubes has an electrical conductivity for direct current (DC) represented as the following percolation formula. That is, DC conductivity increases in an exponential proportion to a difference between a reference content (percolation point) and the CNT content that is higher than the reference content.

[26]
$$\sigma_{DC} = \sigma_0 (P - P_c)^t \text{ (in case of } P > P_c \text{)}$$

[27] where σ_{DC} is DC conductivity, and ' t ' is an experimentally determined value. ' P ' is a volume fraction of multiwalled carbon nanotubes, and P_c is a percolation content (a threshold value for electrical connection, if the CNT content is higher than the percolation content, DC conductivity remarkably changes even with a small change in CNT content). σ_0 is a proportional factor.

[28] FIG. 2 is a graph illustrating the relationship between the CNT content (weight%) and a common logarithm value of electrical conductivity (S/cm) in a conductive paste (hereinafter referred to as a conductive paste of experimental example) containing solely multiwalled carbon nanotubes as a conductor without silver particles. This conductive paste of experimental example uses polyurethane as a binder, and hot-pressed using a hot press to manufacture a paste specimen. The conductive paste of experimental example is not sintered when heated. That is, volatile components, such as a solvent and so on, are just removed from the conductive paste.

[29] It is found from FIG. 2 that it is difficult to obtain a high electrical conductivity of a desired level with solely carbon nanotubes (CNT) as a conductive filler, but that it is possible to form a continuous electrical network with a very low content of carbon nanotubes. As shown in FIG. 2, DC conductivity to CNT content increases most greatly around the fourth data point. And, in the CNT content range of 1 weight% or more, an increase in DC conductivity is insignificant even though the CNT content increases.

[30] From the graph of FIG. 2, the percolation content P_c of carbon nanotubes is determined to 0.0089 weight%, and a point where the electrical conductivity starts to be saturated due to the increased CNT content is about 0.1 to 1 weight% of carbon nanotubes (indicated as a box in FIG. 2). In the percolation formula of the conductive paste of the experimental example, the proportional factor σ_0 is 5.9×10^{-3} S/cm. Theoretically, the proportional factor should be equal to a value of carbon nanotube mat (a similar value to conductivity of copper), however actually the proportional factor is much smaller than a value of carbon nanotube mat as shown in FIG. 2. It is considered that in the conductive paste of the experimental example, a resistivity is not lowered

down to a value of carbon nanotube mat because a continuous network is not formed and the gap is created between the carbon nanotubes, which is not intended to be tied to a specific theory.

- [31] Judging the experimental data, examples and so on, in the conductive paste (not containing silver microparticles) of the present invention, the content of carbon nanotubes is preferably 0.1 to 2.5 weight% based on the total weight of the conductive paste. If the content of carbon nanotubes is less than 0.1 weight%, the electrical conductivity improvement effect does not exhibit. If the content of carbon nanotubes is more than 2.5 weight%, because the electrical conductivity of carbon nanotubes is lower than that of silver particles, the electrical conductivity improvement effect reaches a saturation point. More preferably, the content of carbon nanotubes is 0.5 to 1 weight% in consideration of viscosity, manufacturing cost, conductivity of the conductive paste, and so on.
- [32] The conductive paste of the present invention may use both single-walled nanotubes (SWNT) and multi-walled nanotubes (MWNT) as carbon nanotubes. And, the present invention may use carbon nanotubes, of which the surface is modified by various functional groups. The present invention may use carbon nanotubes produced by thermal chemical vapor deposition, arc discharge and so on. Preferably, the carbon nanotubes have a diameter of 2 to 40 nm. Taking into consideration that silver nanoparticles have a particle size of 1 to 100 nm and silver flake-type particles have a density of 10.5 g/cm³, the carbon nanotubes preferably have a length of 5 to 50 μ m to effectively fill up the gap between silver particles.
- [33] The conductive paste of the present invention comprise 5 to 15 weight% of a binder and a proper content of a solvent. Selectively, the conductive paste may further comprise an additive. For example, the binder may include nitrocellulose, ethyl cellulose, acrylate, acrylate copolymer, polyvinyl-based resin and modified resins thereof. The solvent and the additive may be properly selected from all typical solvents and additives depending on the desired end-use properties with reference to the prior art by an ordinary person skilled in the art. For example, the additive may be at least one selected from the group consisting of a stabilizer, a dispersant, a reducing agent, a surfactant, a wetting agent, a thixotropic agent, a leveling agent, an antifoaming agent, a coupling agent, a surface tension adjusting agent and a thickener, and be preferably included at an amount of 0.1 to 10 weight%.
- [34] According to another aspect of the present invention, a conductive paste contains carbon nanotubes and a silver particle mixture having particle sizes of nanometer and micrometer levels. In the present invention, silver particles having a micrometer level of particle size are hereinafter referred to as silver microparticles. The conductive paste comprises 1 to 10 weight% of silver nanoparticles having an average particles size of 1

to 100 nm, 30 to 60 weight% of silver microparticles having an average particle size larger than 0.1 μm and not exceeding 50 μm , 0.1 to 1 weight% of carbon nanotubes having an average diameter of 2 to 40 nm, 1 to 15 weight% of a binder, based on the total weight of the conductive paste, and a solvent. Selectively, the conductive paste may further comprise an additive. The conductive paste of the present invention can be sintered at a low temperature of 150 $^{\circ}\text{C}$ or less.

- [35] It has been said that silver microparticles are more advantageous than silver nanoparticles in aspects of a paste manufacturing cost and handling and storage stability of particles, but cause an increase in sintering temperature of the conductive paste, and consequently decreases the process efficiency. Generally, a silver paste comprising solely silver flake-type particles having a micrometer level of particle size are sintered to form a continuous electrical network for a desired specific resistivity, when heated at 550 to 700 $^{\circ}\text{C}$ for 30 minutes or longer. Accordingly, to sinter the silver paste at a low temperature, silver particles should have a small particle size. The inventors found that a conductive paste containing silver nanoparticles, silver microparticles and carbon nanotubes at a proper ratio has a low sintering temperature due to the silver nanoparticles, a cost reduction due to the silver microparticles, and improvement in electrical conductivity and a rise in cost reduction due to the carbon nanotubes, and invented a conductive paste containing silver microparticles according to the present invention.
- [36] The conductive paste containing silver microparticles according to another aspect of the present invention may have the same constituent components other than the silver microparticles as the conductive paste containing silver nanoparticles according to an aspect of the present invention. In the conductive paste containing silver microparticles, the content of silver microparticles is 30 to 60 weight%. If the content of silver microparticles is less than 30 weight%, an imperfect electrical network is formed, causing a reduction in electrical conductivity. If the content of silver microparticles is more than 60 weight%, the effect of silver microparticles on silver nanoparticles reduces.
- [37] According to yet another aspect, the present invention provides a conductive circuit board having a circuit wire formed using the conductive paste. A method for fabricating a conductive circuit board is described in brief. A circuit wire is formed by printing the conductive paste on a circuit board made of metal, glass, plastic and so on, by ink jet, spin coating, screen printing and so on. At this time, the circuit wire is formed on a base film that is formed on the surface of the circuit board. The base film of the circuit board may have a circuit pattern scanned thereon in advance by photolithography or screen printing. The conductive paste is sprayed in conformity with the scanned circuit pattern to form a film including a conductive filler. Subsequently,

the circuit board having the conductive paste printed thereon is sintered to remove a solvent and so on, and fuse silver particles. If necessary, a multilayered circuit board may be fabricated through subsequent processes

Mode for the Invention

[38] Hereinafter, the present invention will be described in detail through examples and an exemplary production method. The description proposed herein is just a preferable example for the purpose of illustrations only, not intended to limit the scope of the invention, so it should be understood that other equivalents and modifications could be made thereto without departing from the spirit and scope of the invention.

[39] Conductive pastes of examples according to the present invention and conductive pastes of comparative examples according to the prior art were prepared, and their performance was compared. Methods for preparing the conductive pastes of examples and comparative examples are described below.

[40] **Example 1: Paste containing silver nanoparticles and carbon nanotubes**

[41] 5 g of spherical silver nanoparticles (produced by LS Corp.) having a particle size of 5 to 40 nm, 25 g butyl acetate solution containing nitrocellulose (produced by Korea CnC Co., Ltd., HS 1/2, the solid content of nitrocellulose is 4 g) as a binder, 10 g dispersion containing a propylene glycol methyl ether acetate (PGMA) solvent and carbon nanotubes (the content of carbon nanotubes is 10%, i.e., 1 g, multiwalled, 10 nm diameter, tens of μm length, modification and high-temperature thermal treatment, provided by Korea University), and 60 g silver flake-type microparticles of which D_{50} is 3 μm , were preliminarily mixed and then mix-milled using a three roll mill, so that the silver particles and the carbon nanotubes were sufficiently dispersed. Next, the resultant paste was printed on a PET substrate at a size of 5x5 cm by screen printing using Poly420 (420 meshes). The substrate was sintered at 150 $^{\circ}\text{C}$ for 10 minutes in a convection oven to manufacture a specimen.

[42] **Example 2: Paste containing silver nanoparticles and carbon nanotubes**

[43] An Ag-CNT paste was prepared in the same way as example 1, except that 10 g of silver nanoparticles, 8 g of butyl acetate solution containing nitrocellulose (the solid content of nitrocellulose is 2.4 g), 1 g of carbon nanotubes and 58 g of silver microparticles were used, and 23 g of butyl carbitol acetate (BCA) was added. A substrate was sintered at 140 $^{\circ}\text{C}$ for 4 minutes in a convection oven to manufacture a specimen. FIGs. 3 and 4 are scanning electron microscope (SEM) images of cross section and surface of a circuit electrode formed according to example 2, respectively. As shown in FIG. 3, carbon nanotubes were distributed in the silver nanoparticles to form a denser electrical network. And, as shown in FIG. 4, metallization was accomplished under the sintering conditions of example 2.

[44] **Example 3: Paste containing silver nanoparticles and carbon nanotubes**

[45] An Ag-CNT paste was prepared in the same way as example 1, except that 7 g of silver nanoparticles, 10 g of butyl acetate solution containing nitrocellulose (the solid content of nitrocellulose is 3 g), 2 g of carbon nanotubes and 58 g of silver microparticles were used, and 23 g of butyl carbitol acetate (BCA) was added. A substrate was sintered at 150- °C for 5 minutes in a convection oven to manufacture a specimen.

[46] **Comparative example 1: Paste containing only silver microparticles**

[47] A conductive paste was prepared by mixing a polyurethane binder with 49 to 66 weight% of silver flake-type microparticles (SF-15ED of Ferro Co.) having 1 to 3 μm based on the total weight of the conductive paste, and drying them. The conductive paste was hot-pressed using a hot press to manufacture a specimen.

[48] **Comparative example 2: Paste containing only silver nanoparticles**

[49] A conductive paste was prepared in the same way as example 1, except that 70 g of silver nanoparticles and 30 g of butyl acetate solution containing nitrocellulose (the solid content of nitrocellulose is 5 g) were used, and carbon nanotubes were not added.

[50] **Comparative example 3: Paste containing only carbon nanotubes**

[51] A conductive paste was prepared in the same way as example 1, except that 0.2 weight% of carbon nanotubes were used as a conductive material and silver microparticles were not added.

[52] Table 1 shows the thickness of circuit wires formed using the pastes of examples and comparative examples.

[53] **Method for measuring a specific resistivity**

[54] A specific resistivity was measured using area and thickness by means of a 4-probe tester (LORESTA-GP of Mitsubishi Chemical in Japan) according to the ASTM D 991 specifications. This test was performed by a test method suggested on the operating manual of the tester of Mitsubishi Chemical. Specifically, a surface resistivity was measured and multiplied by a film thickness of the specimen, and the obtained value was determined as a specific resistivity characterized by the ASTM D 991 specifications.

[55] Table 1

[Table 1]

[Table]

	Thicknes s of circuit wire (μm)	Sintering temperatur e ($^{\circ}\text{C}/\text{min}$)	Silver content (weight %)	CNT content(weight%)	Binder content(weight%)	Solvent content(weight%)	Specific re- sistivity ($\Omega\cdot\text{cm}$)
Example 1	3.1	150/10	5	1	4(NC)	30	8.1×10^{-6}
Example 2	3.2	140/4	10	1	2.4(NC)	28.6	6×10^{-6}
Example 3	3.1	150/5	7	2	3(NC)	30	7×10^{-6}
Comparat ive example 1	200	Impossible to sinter at low tem- perature	66	0	34(PU)	0	$\sim 10^{12}$
Comparat ive example 2	3.3	150/5	70	0	9(NC)	21	8.5×10^{-6}
Comparat ive example 3	200	Impossible to sinter at low tem- perature	0	0.2	99.8(PU)	0	2.81×10^5

[56] NC is nitrocellulose, and PU is polyurethane

[57]

[58] As the conductive paste of comparative example 1 contains solely silver particles having a micrometer level of particle size, the conductive paste of comparative example 1 cannot be sintered at a low temperature. The conductive paste of comparative example 1 has a specific resistivity of $\sim 10^{12} \Omega\cdot\text{cm}$, which falls in the specific resistivity range of an insulator. That is, the conductive paste of comparative example 1, in which 49 to 66 weight% of silver microparticles solely are included as a conductive filler, cannot form a continuous electrical network. The specific resistivity of comparative example 1 is higher than a specific resistivity, $10^5 \Omega\cdot\text{cm}$ of the paste of

experimental example shown in FIG. 2, in which solely carbon nanotubes are included as a conductive filler. Thus, the content of silver more than 66 weight% is needed to form a continuous electrical network. Meanwhile, the conductive paste of comparative example 2 is a conventional conductive paste containing silver nanoparticles as the sole conductor. The conductive paste of comparative example 2 has a good specific resistivity of $8.5 \times 10^{-6} \Omega\text{-cm}$, but contains 70 weight% of silver nanoparticles for a high electrical conductivity. Because silver nanoparticles are more expensive than silver microparticles, this high content of silver nanoparticles is not preferable in consideration of economical efficiency for commercialization.

[59] The conductive paste of comparative example 1 contains 66 weight% of silver microparticles, but shows characteristics of an insulator. On the contrary, the conductive paste of comparative example 3 contains 0.2 weight% of carbon nanotubes without silver microparticles, but forms a certain level of conductive network. This means that carbon nanotubes are superior to silver microparticles in forming a conductive network. However, the desired specific resistivity of $10^{-6} \Omega\text{-cm}$ could not be achieved with carbon nanotubes only.

[60] Meanwhile, the conductive pastes of examples 1 to 3 have a low silver content of 5 to 10 weight%, but have a specific resistivity of 6 to $8 \times 10^{-6} \Omega\text{-cm}$, and thus achieve an even higher level of electrical conductivity than conventional pastes. And, the conductive pastes of examples 1 to 3 can be sintered at a low temperature of 140 to 150 °C, at which conventional pastes containing solely silver microparticles cannot be sintered.

[61]

[62] The present invention has been described in detail. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

Claims

- [Claim 1] A conductive paste containing silver nanoparticles, comprising:
based on the total weight of the conductive paste,
15 to 50 weight% of silver nanoparticles having an average particle size of 1 to 100 nm;
0.1 to 2.5 weight% of carbon nanotubes having an average diameter of 2 to 40 nm;
1 to 15 weight% of a binder; and
a solvent.
- [Claim 2] The conductive paste containing silver nanoparticles according to claim 1, further comprising:
0.1 to 10 weight% of at least one additive selected from the group consisting of a stabilizer, a dispersant, a reducing agent, a surfactant, a wetting agent, a thixotropic agent, a leveling agent, an antifoaming agent, a coupling agent, a surface tension adjusting agent and a thickener.
- [Claim 3] The conductive paste containing silver nanoparticles according to claim 1 or 2,
wherein the conductive paste has a sintering temperature of 150 °C or lower.
- [Claim 4] The conductive paste containing silver nanoparticles according to claim 1 or 2,
wherein the conductive paste has a specific resistivity of 2×10^{-6} to $10 \times 10^{-6} \Omega\text{-cm}$.
- [Claim 5] The conductive paste containing silver nanoparticles according to claim 1 or 2,
wherein the carbon nanotubes have an average length of 5 to 50 μm .
- [Claim 6] The conductive paste containing silver nanoparticles according to claim 1 or 2,
wherein the carbon nanotubes are included at an amount of 0.5 to 1 weight%.
- [Claim 7] The conductive paste containing silver nanoparticles according to claim 1 or 2,
wherein the binder is selected from the group consisting of nitro-cellulose, acrylic resin, vinylic resin, ethylcellulose and modified resins thereof.
- [Claim 8] A conductive paste containing silver nanoparticles, comprising:

based on the total weight of the conductive past,

1 to 10 weight% of silver nanoparticles having an average particle size of 1 to 100 nm;

30 to 60 weight% of silver microparticles having an average particle size larger than 0.1 and not exceeding 50 μm ;

0.1 to 1 weight% of carbon nanotubes having an average diameter of 2 to 40 nm;

1 to 15 weight% of a binder; and
a solvent.

[Claim 9] The conductive paste containing silver nanoparticles according to claim 8, further comprising:

0.1 to 10 weight% of at least one additive selected from the group consisting of a stabilizer, a dispersant, a reducing agent, a surfactant, a wetting agent, a thixotropic agent, a leveling agent, an antifoaming agent, a coupling agent, a surface tension adjusting agent and a thickener.

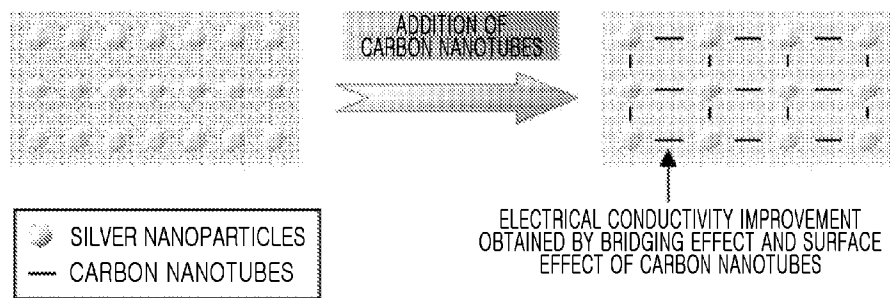
[Claim 10] The conductive paste containing silver nanoparticles according to claim 8 or 9,
wherein the conductive paste has a sintering temperature of 150 $^{\circ}\text{C}$ or lower.

[Claim 11] The conductive paste containing silver nanoparticles according to claim 8 or 9,
wherein the conductive paste has a specific resistivity of 2×10^{-6} to $10 \times 10^{-6} \Omega\text{-cm}$.

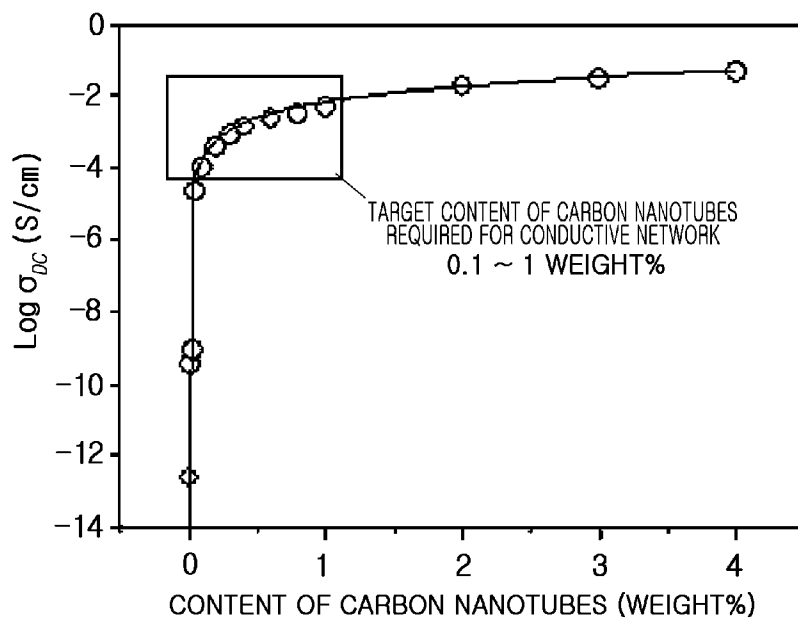
[Claim 12] The conductive paste containing silver nanoparticles according to claim 8 or 9,
wherein the carbon nanotubes have an average length of 5 to 50 μm .

[Claim 13] A conductive circuit board having a circuit wire formed from the conductive paste defined in claim 1 or 8.

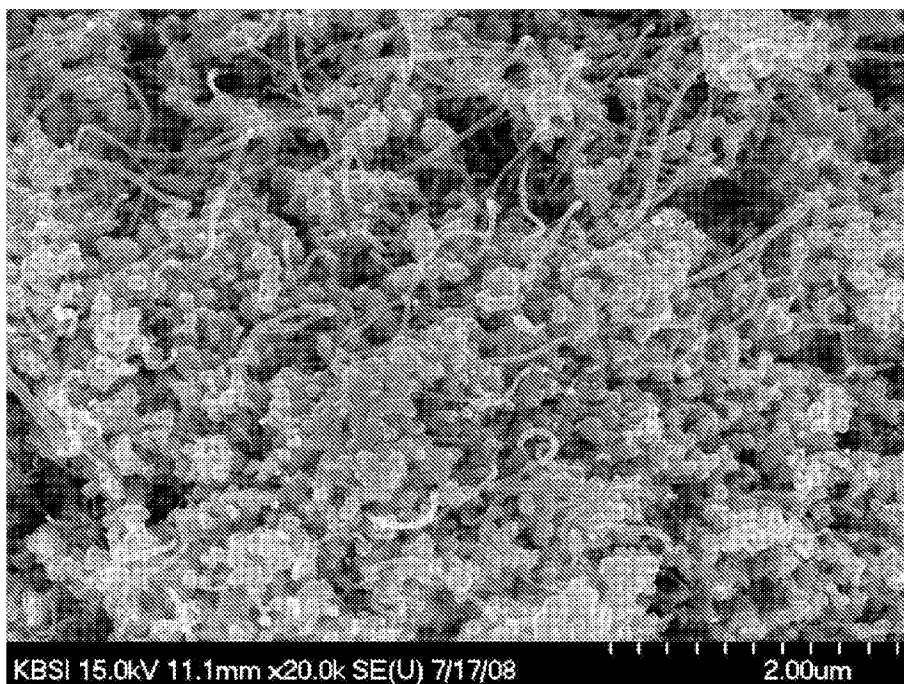
[Fig. 1]



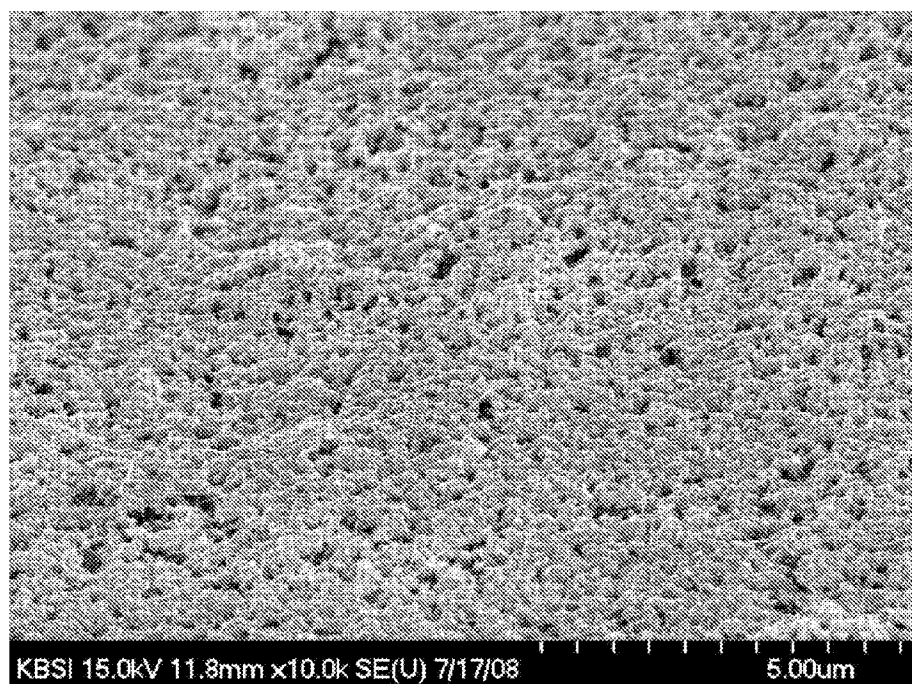
[Fig. 2]



[Fig. 3]



[Fig. 4]



A. CLASSIFICATION OF SUBJECT MATTER**HOIB I/16(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC HOIB

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

(Chinese Patents and application for patent)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KPA, PAJ, FPD, USPATFULL) in KIPO, CA online & keywords: conductive, paste, silver, carbon nanotube

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 10-2007-0059914 A (ELECTRONICS AND TELECOMMUNICATIONS RESEARCH INSTITUTE) 12 June 2007 See the abstract; claims 1, 6-11	1-13
A	KR 10-2008-0078397 A (LG ELECTRONICS INC.) 27 August 2008 See the abstract; claims 1-9	1-13
A	JP 2006-140206 A (SUMITOMO METAL MINING ∞ LTD.) 01 June 2006 See the whole document	1-13
A	JP 2007-149522 A (SUMITOMO METAL MINING CO LTD.) 14 June 2007 See the whole document	1-13

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

07 MAY 2010 (07.05.2010)

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No
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