

DESCRIPTION

TITLE

SILVER POWDER AND RESIN-CURABLE CONDUCTIVE PASTE

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TECHNICAL FIELD

[0001] The present disclosure relates to a silver powder and a resin-curable conductive paste.

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BACKGROUND

[0002] In recent years, heterojunction (HJT) type solar cells have attracted attention. In HJT type solar cells and the like, electrodes and conductor patterns are typically formed by firing and curing a resin-curable conductive paste using silver powder at a relatively low temperature of about 200 °C in an air atmosphere.

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[0003] For example, JP 2013-159805 A (PTL 1) proposes fine silver particles obtained by a predetermined production method and having an average particle diameter (D_{SEM}) of 30 nm to 100 nm and a tap density of 3.0 g/cm³ or more, and describes that such fine silver particles are used in resin-curable conductive pastes and the like.

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CITATION LIST

Patent Literature

[0004] PTL 1: JP 2013-159805 A

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SUMMARY

(Technical Problem)

[0005] When the firing temperature for forming electrodes, conductor patterns, etc. is lowered, the resistance value may increase. It is thus desirable that a conductive paste containing silver powder suppresses an increase in volume resistivity even when the firing temperature is lowered, and has low volume resistivity even when fired at a low temperature of 150 °C to 200 °C.

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[0006] It could therefore be helpful to provide a silver powder capable of, in the case of being formed into a conductive paste, imparting low volume resistivity even when fired at low temperatures.

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It could also be helpful to provide a resin-curable conductive paste

capable of achieving low volume resistivity even when fired at low temperatures.

(Solution to Problem)

5 [0007] Intensive studies made to achieve the objects stated above led to the present disclosure.

[0008] We thus provide the following.

[0009] [1] A silver powder comprising: a surface treatment agent; a ratio of oxygen content to BET specific surface area of 0.11 or more; and a crystallite diameter of 30 nm or more and 38 nm or less.

10 [0010] [2] The silver powder according to [1], comprising a ratio of Ig-loss to the BET specific surface area of 0.51 or more.

[0011] [3] The silver powder according to [1] or [2], comprising: a volume-based cumulative 50 % diameter D_{50} measured by a laser diffraction method of 0.1 μm or more and 1.0 μm or less; and a volume-based cumulative 90 % diameter D_{90} measured by the laser diffraction method of 1.2 μm or less.

[0012] [4] The silver powder according to any one of [1] to [3], wherein the BET specific surface area is 0.90 m^2/g or more and 2.50 m^2/g or less.

[0013] [5] The silver powder according to any one of [1] to [4], for use in a resin-curable conductive paste.

20 [0014] [6] A resin-curable conductive paste comprising the silver powder according to any one of [1] to [4].

(Advantageous Effect)

[0015] It is thus possible to provide a silver powder capable of, in the case of being formed into a conductive paste, imparting low volume resistivity even
25 when fired at low temperatures.

It is also possible to provide a resin-curable conductive paste capable of achieving low volume resistivity even when fired at low temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

30 [0016] In the accompanying drawings:

FIG. 1 is an external perspective view of an example of a silver powder production device;

FIG. 2A is a sectional view perpendicular to the flow path of a silver complex solution at the center position of each reducing agent supply pipe of a reducing agent addition member in the silver powder production device;
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FIG. 2B is a sectional view taken along line A-A in FIG. 2A in a

direction horizontal to the flow path of the silver complex solution;

FIG. 2C is a sectional view taken along line B-B in FIG. 2A in a direction horizontal to the flow path of the silver complex solution;

FIG. 3 is an SEM photograph (20,000x magnification) of the silver powder according to Example 1;

FIG. 4 is an SEM photograph (20,000x magnification) of the silver powder according to Example 2;

FIG. 5 is an SEM photograph (20,000x magnification) of the silver powder according to Example 3;

FIG. 6 is an SEM photograph (20,000x magnification) of the silver powder according to Example 4;

FIG. 7 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 1; and

FIG. 8 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 2.

DETAILED DESCRIPTION

[0017] (Terminology and Measurement Methods)

Prior to describing embodiments, terminology, measurement methods, and the like used in this specification will be explained.

[0018] <BET Specific Surface Area>

In this specification, the BET specific surface area was measured by single-point BET method based on nitrogen adsorption using Macsorb HM-model 1210 (produced by Mountech Co., Ltd.). The BET specific surface area was measured using a 3.0 g sample weight and an N₂/He (30/70) mixed gas at a gas flow rate of 25 mL/min. The degassing conditions before measurement were 60 °C for 10 minutes.

[0019] <Crystallite Diameter>

The crystallite diameter D_x was determined using an X-ray diffractometer (SmartLab produced by Rigaku Corporation) according to the Scherrer formula ($D_{hkl} = K\lambda/\beta\cos\theta$). In the Scherrer formula, D_{hkl} denotes the crystallite diameter (the size of the crystallite in a direction perpendicular to hkl) (unit: nm), λ denotes the wavelength of the measured X-ray (0.15405 nm when using a Cu target), β denotes the broadening (rad) of the diffraction line due to the crystallite diameter (expressed using the full width at half maximum), θ denotes the Bragg angle (rad) of the diffraction angle (the angle at which the

angle of incidence and the angle of reflection are equal, using the peak top angle), and K denotes the Scherrer constant ($K = 0.94$). The calculation may use peak data of the Miller index (111) plane.

[0020] <Carbon Content and Oxygen Content of Silver Powder>

5 In this specification, the carbon content of silver powder was determined using a carbon/sulfur analyzer (EMIA-810W produced by HORIBA, Ltd.). Specifically, 0.07 g of a sample (silver powder) was heated to 1350 °C in an oxygen gas stream and melted, CO and CO₂ generated as a result were measured by an infrared absorption method, and the carbon content was
10 calculated from the measured values.

 The oxygen content of silver powder was determined using an oxygen/nitrogen/hydrogen simultaneous analyzer (ONH836 produced by LECO Corporation). Specifically, the oxygen content in 0.05 g of a sample (silver powder) was measured by an infrared absorption method in an Ar gas
15 atmosphere with the power of an impulse furnace set to 3500 W.

[0021] <Quantification of Surface Treatment Agent>

 In this specification, for example, in the case where a surface treatment agent of silver powder is a fatty acid such as stearic acid, the content of the fatty acid was measured according to the fatty acid quantitative analysis
20 method described in JP 5622543 B2.

 Specifically, the silver powder was first dissolved in nitric acid, and then an organic solvent (n-hexane) was mixed. The entire amount of the surface treatment agent was extracted into the organic solvent phase. A predetermined amount of the organic solvent phase was then collected, and the organic solvent
25 was evaporated to dryness. The remaining solid was subjected to carbon content measurement using a carbon-sulfur analyzer, and the content of the fatty acid was calculated based on the measured carbon amount.

[0022] In this specification, for example, in the case where the surface treatment agent of silver powder is benzotriazole, the content of benzotriazole
30 was measured according to the quantitative analysis method for benzotriazole and benzotriazole salts described in JP 5523153 B2. Specifically, the silver powder was first washed with a hydrochloric acid aqueous solution, and the washings were quantitatively analyzed by an absorptiometric method to determine the content of benzotriazole.

35 **[0023]** The type of surface treatment agent can be identified by qualitative analysis using gas chromatography of the surface treatment agent volatilized

by heating the silver powder.

[0024] <True Density>

The true density was measured as follows. Silver powder was placed in a 10 cc platinum crucible, and the mass of the placed silver powder was precisely measured. The volume of the mass-measured silver powder was then measured using a dry automatic density meter (AccuPyc II 1340 produced by Micromeritics) by the constant volume expansion method (referred to as the “gas pycnometer method” in the Japanese Pharmacopoeia), and the density was calculated. The true density measurement includes the closed voids inside the silver particles that are not connected to the outside.

[0025] <Average Primary Particle Diameter D_{SEM} >

The average primary particle diameter D_{SEM} (hereinafter also simply referred to as “ D_{SEM} ”) was determined by measuring the equivalent circle diameters (Heywood diameters) of any 100 or more silver particles in a SEM image of silver powder and calculating the average value. D_{SEM} can be obtained, for example, using images taken at 10,000x magnification and image shape measurement software such as Mac-View (produced by Mountech Co., Ltd.).

[0026] <Particle Size Distribution>

In this specification, the volume-based cumulative 10 % particle diameter D_{10} , cumulative 50 % particle diameter D_{50} , and cumulative 90 % particle diameter D_{90} of silver powder were measured using a laser diffraction/scattering particle size distribution measurement device (MICROTRAC MT-3300 EXII produced by MicrotracBEL Corp.). For measurement, 0.1 g of a sample (silver powder) was added to 40 mL of isopropyl alcohol (IPA) and dispersed. Dispersion was performed using an ultrasonic homogenizer (US-150T produced by Nihonseiki Kaisha Ltd., 19.5 kHz, tip diameter 18 mm). The dispersion time was 2 minutes. The sample that had undergone the dispersion was supplied to the foregoing device, and the particle size distribution was determined using the attached analysis software.

Hereinafter, the volume-based cumulative 10 % particle diameter D_{10} , cumulative 50 % particle diameter D_{50} , and cumulative 90 % particle diameter D_{90} measured by the laser diffraction method may be simply referred to as “ D_{10} ,” “ D_{50} ,” and “ D_{90} ,” respectively.

[0027] <Ignition Loss (Ig-loss) Value>

In this specification, the term “ignition loss (Ig-loss) value” refers to the amount of mass change when heated from room temperature to 800 °C.

Specifically, the ignition loss (Ig-loss) value serves as an indicator of the amount of non-silver components contained in the silver powder, and indicates the amount of residual components remaining in the silver powder, such as processing agents and additives used in the silver powder production process.

- 5 In this specification, the ignition loss (Ig-loss) value was calculated as follows: A silver powder sample was precisely weighed (weight: w_1) and placed in a magnetic crucible, heated to 800 °C, and held at 800 °C for 30 minutes as a sufficient time to reach constant weight. The sample was then cooled and weighed again (weight: w_2), and the ignition loss (Ig-loss) value was calculated
10 using the following formula: Ignition loss (Ig-loss) value (mass%) = $(w_1 - w_2)/w_1 \times 100$.

[0028] (Silver Powder)

- A silver powder according to the present disclosure comprises: a surface treatment agent; a ratio of oxygen content to BET specific surface area
15 (“oxygen content of silver powder”/“BET specific surface area”) of 0.11 or more; and a crystallite diameter of 30 nm or more and 38 nm or less. Here, the ratio of oxygen content to BET specific surface area refers to a value obtained by dividing the oxygen content in the silver powder (expressed in mass%) by the BET specific surface area of the silver powder (expressed in m^2/g).
20 Although the unit of “oxygen content of silver powder”/“BET specific surface area” is omitted in this specification, the unit is “mass%·g/ m^2 .”

- Such silver powder, in the case of being formed into a conductive paste, can impart low volume resistivity even when fired at low temperatures. The reason for this is presumed to be the following. When resin-curing firing is
25 performed at low temperatures such as 200 °C, the amount of heat required to cause necking between silver particles may be insufficient. A higher oxygen content per specific surface area promotes combustion of the surface treatment agent and the like on the silver particle surface, thereby compensating for the required amount of heat.

- 30 **[0029]** The crystallite diameter is 30 nm or more, and preferably 32 nm or more. The crystallite diameter is 38 nm or less.

- If the crystallite diameter is within the above range, necking between silver particles readily progresses. The silver powder can thus be expected to, in the case of being formed into a conductive paste, impart low volume
35 resistivity even when fired at low temperatures.

[0030] The ratio of oxygen content to BET specific surface area is 0.11 or

more, and preferably 0.12 or more. Here, the oxygen content relative to the BET specific surface area refers to a value obtained by dividing the oxygen content (expressed in mass%) by the specific surface area (expressed in m^2/g).

If the ratio of oxygen content to BET specific surface area is 0.11 or
5 more, combustion of the silver particle surface can be promoted.

The ratio of oxygen content to BET specific surface area is, for example, preferably 0.60 or less, and more preferably 0.50 or less. If the ratio is more than 0.60, there is a risk of adverse effects due to the generation of voids caused by gas evolution or shrinkage.

10 **[0031]** The oxygen content of the silver powder is preferably 0.13 mass% or more, and more preferably 0.14 mass% or more. The oxygen content of the silver powder is preferably 0.80 mass% or less, and more preferably 0.50 mass% or less.

[0032] The carbon content of the silver powder is preferably 0.38 mass% or
15 more, and more preferably 0.40 mass% or more. The carbon content of the silver powder is preferably 1.00 mass% or less, and more preferably 0.70 mass% or less.

If the carbon content of the silver powder is 0.38 mass% or more, combustion of the silver particle surface can be promoted together with the
20 aforementioned oxygen.

If the carbon content of the silver powder is more than 1.00 mass%, there is a risk of adverse effects due to the generation of voids caused by gas evolution or shrinkage.

[0033] The BET specific surface area is preferably 0.90 m^2/g or more, more
25 preferably 1.00 m^2/g or more, further preferably 1.05 m^2/g or more, and even more preferably 1.10 m^2/g or more. The BET specific surface area is preferably 2.50 m^2/g or less, more preferably 2.25 m^2/g or less, further preferably 2.00 m^2/g or less, and even more preferably 1.80 m^2/g or less.

If the BET specific surface area is 0.90 m^2/g or more, appropriate
30 particle activity can be obtained, which is advantageous in terms of the volume resistivity of wiring patterns formed using the conductive paste even when fired at low temperatures. In addition, higher density can be readily achieved.

A BET specific surface area of 2.50 m^2/g or less is advantageous in terms of ease of handling of the conductive paste formed from the silver powder.

35 **[0040]** D_{50} is 0.1 μm or more, preferably 0.25 μm or more, more preferably 0.30 μm or more, and further preferably 0.35 μm or more. D_{50} is 1.0 μm or less,

preferably 0.9 μm or less, and more preferably 0.8 μm or less. If D_{50} is within the above range, fine-line printing is possible when the silver powder is used in a conductive paste, and the fine-line printability of the conductive paste can be improved. In the case where emphasis is placed on achieving high conductivity of a conductive film obtained by low-temperature firing of a resin-curable conductive paste using the silver powder according to the present disclosure, D_{50} of the silver powder according to the present disclosure may be 0.1 μm or more and 0.55 μm or less, and may be 0.2 μm or more and 0.5 μm or less.

5 **[0035]** D_{10} is preferably 0.05 μm or more, and more preferably 0.10 μm or more. D_{10} is preferably 0.40 μm or less, and more preferably 0.35 μm or less.

If D_{10} is within the above range, the fine-line printability of the conductive paste can be improved.

[0036] D_{90} is preferably 0.5 μm or more, and more preferably 0.6 μm or more.

15 D_{90} is preferably 1.2 μm or less, and more preferably 1.1 μm or less.

If D_{90} is within the above range, the fine-line printability of the conductive paste can be improved.

[0037] In one embodiment, the silver powder preferably has D_{50} of 0.1 μm or more and 1.0 μm or less and D_{90} of 1.2 μm or less.

20 Such silver powder can effectively improve the fine-line printability of the conductive paste.

[0038] The true density of silver is 10.49 g/cm^3 . The true density of the silver powder according to the present disclosure is, for example, 9.8 g/cm^3 or more and 10.49 g/cm^3 or less, and may be 9.9 g/cm^3 or more.

25 **[0039]** D_{SEM} is preferably 0.10 μm or more, more preferably 0.20 μm or more, further preferably 0.25 μm or more, and even more preferably 0.35 μm or more. D_{SEM} is preferably 1.00 μm or less, more preferably 0.90 μm or less, and further preferably 0.80 μm or less. If D_{SEM} is within the above range, the fine-line printability of the conductive paste can be effectively improved. In the case where emphasis is placed on achieving high conductivity of a conductive film obtained by low-temperature firing of a resin-curable conductive paste using the silver powder according to the present disclosure, D_{SEM} of the silver powder according to the present disclosure may be 0.10 μm or more and 0.4 μm or less, and may be 0.20 μm or more and 0.35 μm or less.

35 **[0040]** The ignition loss (Ig-loss) value is preferably 0.3 mass% or more, and more preferably 0.35 mass% or more. The ignition loss (Ig-loss) value is

preferably 1.2 mass% or less, more preferably 1.1 mass% or less, further preferably 0.95 mass% or less, and even more preferably 0.8 mass% or less. If the ignition loss value is 0.3 mass% or more, agglomeration of silver powder particles can be suppressed and dispersibility can be improved. If the ignition
5 loss value is less than 1.2 mass%, deterioration of resistance due to excessive impurities can be prevented. In the case where emphasis is placed on achieving high conductivity of a conductive film obtained by low-temperature firing of a resin-curable conductive paste using the silver powder according to the present disclosure, the ignition loss value of the silver powder according to the present
10 disclosure may be 0.65 mass% or more and 1.2 mass% or less, and may be 0.7 mass% or more and 1.2 mass% or less.

[0041] The ratio of the ignition loss (Ig-loss) value to the BET specific surface area (“Ig-loss”/“BET specific surface area”) is preferably 0.51 or more, and more preferably 0.52 or more. The ratio of the ignition loss (Ig-loss) value to
15 the BET specific surface area is preferably 1.0 or less, and more preferably 0.8 or less. Here, the ratio of the ignition loss (Ig-loss) value to the BET specific surface area refers to a value obtained by dividing the ignition loss (Ig-loss) value of the silver powder (expressed in mass%) by the BET specific surface area of the silver powder (expressed in m^2/g). Although the unit of “Ig-loss”/“BET specific surface area” is omitted in this specification, the unit is
20 “mass%·g/ m^2 .”

If “Ig-loss”/“BET specific surface area” is 0.51 or more, combustion of the silver particle surface can be promoted.

If “Ig-loss”/“BET specific surface area” is more than 1.0, there is a risk
25 of adverse effects due to the generation of voids caused by gas evolution or shrinkage.

[0042] The silver powder according to the present disclosure contains a surface treatment agent.

Specific examples of the surface treatment agent will be described in
30 the “Silver Powder Production Method” section below.

[0043] The silver powder according to the present disclosure can be used, without particular limitation, in conductive pastes such as resin-curable conductive pastes and sinterable conductive pastes. Given that the silver powder according to the present disclosure can provide low volume resistivity
35 even when fired at low temperatures, the silver powder according to the present disclosure is suitable for use in resin-curable conductive pastes.

[0044] (Silver Powder Production Method)

The method of producing the silver powder according to the present disclosure is not particularly limited. For example, the silver powder according to the present disclosure can be produced by a method including: flowing a
5 silver-containing solution through a flow path; adding a pH adjuster to the flow path at a pH adjuster addition position midway through the flow path; adding a complexing agent to the flow path at a complexing agent addition position downstream of the pH adjuster addition position; adding hydrazine to the flow path at a reducing agent addition position downstream of the complexing agent
10 addition position; and reducing and precipitating silver powder in the flow path.

In this silver powder production method, the silver-containing solution, the pH adjuster, the complexing agent, and the hydrazine-based reducing agent are continuously supplied in this order and quantitatively mixed, thereby maintaining constant the rate of silver complex formation and the rate of
15 reduction precipitation of silver powder. This enables quantitative and continuous production of predetermined silver powder.

[0045] The silver-containing solution is a solution that reacts with the complexing agent to form a silver complex, and a solution containing a silver salt can be used. Examples thereof include aqueous solutions of silver nitrate,
20 silver chloride, silver formate, silver oxalate, and silver sulfate. From the viewpoint of availability, etc., a silver nitrate aqueous solution is preferred.

[0046] The silver concentration of the silver-containing solution is preferably 0.01 mol/L or more and more preferably 0.05 mol/L or more, from an economic viewpoint.

25 The silver concentration of the silver-containing solution is preferably 0.5 mol/L or less and more preferably 0.3 mol/L or less, from the viewpoint of ensuring interparticle distance after reduction precipitation and suppressing agglomeration.

[0047] In this embodiment, the term “flow velocity” refers to a value obtained
30 by dividing the flow rate of the solution by the cross-sectional area of the pipe, assuming that the pipe is filled with liquid. The elapsed time between specific positions is calculated by dividing the length between the positions by the flow velocity. The flow velocity of the silver-containing solution is preferably 0.45 m/sec or more, more preferably 0.65 m/sec or more, and further preferably 1.00
35 m/sec or more, from the viewpoints of productivity and forming monodisperse particles. The flow velocity of the silver-containing solution is preferably 3.20

m/sec or less, more preferably 2.70 m/sec or less, and further preferably 2.00 m/sec or less, from the viewpoints of suppressing agglomeration and forming monodisperse particles.

5 **[0048]** In the foregoing silver paste production method, the silver-containing solution is flown through the flow path, and the pH adjuster is added to the flow path at the pH adjuster addition position midway through the flow path to adjust the pH of the silver-containing solution. Thus, the particle diameter of the silver powder can be adjusted effectively. As the pH adjuster, common alkaline or acidic pH adjusters such as sodium hydroxide, potassium hydroxide,
10 sodium carbonate, and nitric acid can be used.

The pH adjuster is typically added to the flow path in the form of a pH adjuster aqueous solution. The amount of the pH adjuster added is appropriately adjusted depending on the particle diameter of the silver powder to be produced.

15 **[0049]** In the foregoing silver paste production method, the complexing agent is added to the flow path at the complexing agent addition position downstream of the pH adjuster addition position, to form a silver complex.

The complexing agent is typically added to the flow path in the form of a complexing agent aqueous solution.

20 **[0050]** Examples of the complexing agent include ammonia, ammonium salts, citric acid, and acetic acid. Among these, ammonia is preferred. Ammonia can be added in the form of ammonia water.

For example, in the case where ammonia water is added as a complexing agent, a silver ammine complex is formed. The silver ammine
25 complex is preferred because it can be easily reduced by hydrazine.

[0051] The concentration of ammonia water is preferably 0.35 mol/L or more and more preferably 0.50 mol/L or more, and preferably 16.2 mol/L or less, more preferably 15.1 mol/L or less, and further preferably 10.0 mol/L or less, from an economic viewpoint.

30 **[0052]** The amount of ammonia added per 1 mol of silver is preferably 2.10 mol or more, and more preferably 2.20 mol or more.

The amount of ammonia added per 1 mol of silver is preferably 10.00 mol or less, and more preferably 8.00 mol or less.

[0053] The flow velocity of the complexing agent added at the complexing agent addition position is preferably 0.40 m/sec or more, more preferably 0.60
35 m/sec or more, and further preferably 1.00 m/sec or more, and preferably 3.20

m/sec or less, more preferably 2.70 m/sec or less, and further preferably 2.00 m/sec or less.

[0054] In the case where a complexing agent other than ammonia is used, too, the concentration, amount added, and flow rate may be set in the same way as
5 above, taking into consideration the amount of the complexing agent relative to the amount of silver required to form the complex.

[0055] In the foregoing silver paste production method, the hydrazine-based reducing agent is added to the flow path at the reducing agent addition position downstream of the complexing agent addition position, thereby reducing and
10 precipitating silver powder.

Examples of the hydrazine-based reducing agent include hydrazine, hydrazine hydrate, hydrazine carbonate, hydrazine sulfate, and phenylhydrazine. Among these, hydrazine and hydrazine carbonate are preferred, and hydrazine is more preferred. Using hydrazine enables stable
15 production of silver powder with a desired particle diameter. The hydrazine-based reducing agent is typically added to the flow path in the form of an aqueous solution.

[0056] The concentration of hydrazine in the hydrazine aqueous solution is preferably 0.025 mol/L or more, more preferably 0.05 mol/L or more, and
20 further preferably 0.10 mol/L or more, and preferably 3.3 mol/L or less, more preferably 2.0 mol/L or less, and further preferably 1.0 mol/L or less, from the viewpoint of ensuring a uniform reduction reaction.

The concentration of the hydrazine-based reducing agent in the hydrazine-based reducing agent aqueous solution is preferably 0.025 mol/L or
25 more, more preferably 0.05 mol/L or more, further preferably 0.10 mol/L or more, and preferably 3.3 mol/L or less, more preferably 2.0 mol/L or less, and further preferably 1.0 mol/L or less, from the viewpoint of ensuring a uniform reduction reaction.

[0057] The amount of hydrazine added per 1 mol of silver is preferably 0.26
30 mol or more and more preferably 0.28 mol or more, so that substantially no unreacted silver is generated.

The amount of hydrazine added per 1 mol of silver is preferably 0.88 mol or less, more preferably 0.75 mol or less, and further preferably 0.50 mol or less, in order to avoid adding an excessive amount of reducing agent.

35 The amount of the hydrazine-based reducing agent added per 1 mol of silver is preferably 0.26 mol or more and more preferably 0.28 mol or more,

so that substantially no unreacted silver is generated.

The amount of the hydrazine-based reducing agent added per 1 mol of silver is preferably 0.88 mol or less, more preferably 0.75 mol or less, and further preferably 0.50 mol or less, in order to avoid adding an excessive amount of reducing agent.

[0058] In the foregoing silver paste production method, the flow velocity of the silver complex solution immediately before the addition of the reducing agent to the flow path is preferably 0.50 m/sec or more, more preferably 0.75 m/sec or more, and further preferably 1.0 m/sec or more, from the viewpoint of productivity. The flow velocity of the silver complex solution is preferably 3.5 m/sec or less, more preferably 3.0 m/sec or less, and further preferably 2.0 m/sec or less, from the viewpoint of suppressing agglomeration and forming monodisperse particles.

[0059] The flow velocity of the reducing agent when added to the flow path is preferably not less than 0.5 times and more preferably not less than 0.8 times the flow velocity of the silver complex solution immediately before the addition of the reducing agent. The flow velocity of the reducing agent when added to the flow path is preferably no more than 2.5 times, more preferably no more than 2.0 times, and further preferably no more than 1.5 times the flow velocity of the silver complex solution immediately before the addition of the reducing agent, from the viewpoint of suppressing an excessive increase in liquid flow toward the pipe wall and preventing a reduction in mixing efficiency.

[0060] In the foregoing silver paste production method, given that the hydrazine-based reducing agent is added after the formation of the silver complex, the time required for the silver-containing solution to flow from the complexing agent addition position to the reducing agent addition position (i.e., the elapsed time calculated by dividing the length from the complexing agent addition position to the reducing agent addition position by the flow velocity of the silver complex solution immediately before the addition of the reducing agent) is preferably 0.1 seconds or more, and more preferably 0.5 seconds or more.

On the other hand, as the time elapsed from the formation of the complex increases, the stability of the silver complex may increase and the reduction reaction may not proceed as easily. Hence, to ensure the freshness of the silver complex at the time of addition of the reducing agent, the elapsed

time is preferably 10.0 seconds or less, and more preferably 5.0 seconds or less.

[0061] In the foregoing silver paste production method, a surface treatment agent may be added to the flow path between the complexing agent addition position and the reducing agent addition position, or downstream of the reducing agent addition position. Adding a surface treatment agent is advantageous in suppressing agglomeration of the reduced and precipitated silver powder. The surface treatment agent is preferably added between the complexing agent addition position and the reducing agent addition position.

[0062] Examples of the surface treatment agent include fatty acids, fatty acid salts, surfactants, organic metals, chelating agents, and protective colloids. The surface treatment agent may be used in an amount of 0.3 mass% or more and 1.3 mass% or less relative to the silver in the silver-containing solution. The surface treatment agent may be used in the form of an emulsion, solution, etc.

[0063] (1) Fatty Acids

Examples of fatty acids include propionic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, acrylic acid, oleic acid, linoleic acid, arachidonic acid, and ricinoleic acid.

[0064] (2) Fatty Acid Salts

Examples of fatty acid salts include metal salts of the fatty acids listed above in (1). Examples of metals include lithium, sodium, potassium, barium, magnesium, calcium, aluminum, iron, cobalt, manganese, lead, zinc, tin, strontium, zirconium, silver, and copper.

[0065] (3) Surfactants

Examples of surfactants include anionic surfactants such as alkylbenzene sulfonates and polyoxyethylene alkyl ether phosphates; cationic surfactants such as aliphatic quaternary ammonium salts; amphoteric surfactants such as imidazolinium betaine; and nonionic surfactants such as polyoxyethylene alkyl ethers and polyoxyethylene fatty acid esters.

[0066] Examples of organic metals include acetylacetonate tributoxyzirconium, magnesium citrate, diethylzinc, dibutyltin oxide, dimethylzinc, tetra-n-butoxyzirconium, triethylindium, triethylgallium, trimethylindium, trimethylgallium, monobutyltin oxide, tetraisocyanate silane, tetramethylsilane, tetramethoxysilane, monomethyltriisocyanate silane, silane coupling agents, titanate-based coupling agents, and aluminum-based coupling agents.

[0067] (5) Chelating Agents

Examples of chelating agents include imidazole, oxazole, thiazole, selenazole, pyrazole, isoxazole, isothiazole, 1H-1,2,3-triazole, 2H-1,2,3-triazole, 1H-1,2,4-triazole, 4H-1,2,4-triazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1H-1,2,3,4-tetrazole, 1,2,3,4-oxatriazole, 1,2,3,4-thiatriazole, 2H-1,2,3,4-tetrazole, 1,2,3,5-oxatriazole, 1,2,3,5-thiatriazole, indazole, benzimidazole, and benzotriazole; salts of these chelating agents; and polycarboxylic acids including dicarboxylic acids such as succinic acid, malonic acid, glutaric acid, and adipic acid.

10 **[0068]** (6) Protective Colloids

Examples of protective colloids include peptides, gelatin, albumin, gum arabic, protalbinic acid, lysalbinic acid, and glue.

[0069] Among the surface treatment agents, (1) fatty acids are preferred, with stearic acid being particularly preferred, from the viewpoint of ease of
15 modifying the silver particle surface. (1) Fatty acids are preferably in the form of emulsions, such as stearic acid emulsions.

[0070] In the foregoing silver paste production method, the temperature of the silver complex solution immediately before the addition of the reducing agent is preferably 20 °C or higher and more preferably 30 °C or higher, from the
20 viewpoint of reactivity in the reduction reaction.

The temperature of the liquid flowing through the flow path is preferably 65 °C or lower and more preferably 60 °C or lower, from the viewpoint of operability.

[0071] In the foregoing silver paste production method, liquid mixing may be
25 performed by applying helical rotation in the axial direction of the flow path using a mixer.

[0072] In the foregoing silver paste production method, silver powder can be obtained by discharging the liquid containing the reduced and precipitated silver powder (hereinafter also referred to as “silver powder-containing
30 liquid”) out of the flow path and collecting it.

The silver powder-containing liquid is typically obtained in the form of a slurry or dispersion.

[0073] The time from the addition of the reducing agent to the discharge of the silver powder-containing liquid out of the flow path is preferably 1 second
35 or more and more preferably 2 seconds or more, from the viewpoint of allowing for the completion of the reduction reaction.

The time from the addition of the reducing agent to the discharge of the silver powder-containing liquid out of the flow path is preferably 10 seconds or less and more preferably 5 seconds or less, from the viewpoint of suppressing adhesion to the piping.

- 5 **[0074]** By filtering and washing with water the silver powder-containing liquid discharged out of the flow path, a cake containing silver powder and water and having almost no fluidity is obtained.

The cake is dried using a dryer such as a forced-circulation atmospheric dryer, vacuum dryer, or flash dryer, as a result of which predetermined silver
10 powder is obtained. Drying can be accelerated by replacing the moisture in the cake with a lower alcohol or the like.

The cake may be subjected to dry disintegration treatment, surface smoothing treatment, and the like. The dry disintegration treatment can be carried out, for example, using a sample mill, blender, coffee mill, or multi-
15 purpose mixer. The surface smoothing treatment can be carried out by mechanically causing particles to collide with each other using a high-speed stirrer.

After this, agglomerates of silver powder larger than a predetermined particle diameter may be removed by classification treatment.

- 20 The cake may be dried, crushed, and classified using an all-in-one device capable of drying, disintegration, and classification (such as Drymeister or Micron Dryer produced by Hosokawa Micron Corporation).

[0075] An example of a silver powder production device that can be used in the foregoing silver powder production method will be described below with
25 reference to the drawings, although the foregoing silver powder production method is not limited to using such a silver powder production device.

An example of a silver powder production device that can be used in the production method according to the present disclosure will be described below with reference to the drawings.

- 30 **[0076]** FIG. 1 is an external perspective view of an example of a silver powder production device.

In FIG. 1, a silver powder production device 1 includes a pipe 2 through which a silver-containing solution flows, a pH adjuster supply pipe 7 that supplies a pH adjuster, a complexing agent supply pipe 6 that is located
35 downstream of the pH adjuster supply pipe 7 and supplies a complexing agent, a surface treatment agent supply pipe 5 that is located downstream of the

complexing agent supply pipe 6 and supplies a surface treatment agent, and a reducing agent addition member 10 that is located downstream of the surface treatment agent supply pipe 5 and supplies a hydrazine-based reducing agent as a reducing agent. Reducing agent supply pipes 4a and 4b are eccentrically
5 connected to the reducing agent addition member 10. In the silver powder production device 1 in FIG. 1, the surface treatment agent supply pipe 5 is located between the complexing agent supply pipe 6 and the reducing agent addition member 10. Alternatively, the surface treatment agent supply pipe 5 may be located downstream of the reducing agent addition member 10.

10 **[0077]** FIG. 2A is a sectional view perpendicular to the flow path of the silver complex solution at the center positions of the reducing agent supply pipes 4a and 4b of the reducing agent addition member 10 in FIG. 1. FIG. 2B is a sectional view taken along line A-A in FIG. 2A in a direction horizontal to the flow path of the silver complex solution. FIG. 2C is a sectional view taken
15 along line B-B in FIG. 2A in a direction horizontal to the flow path of the silver complex solution.

[0078] In FIG. 2A, a gap 13 is provided along the outer periphery of the pipe 2 that serves as the flow path of the silver complex solution, and the gap 13 is connected to the interiors of the reducing agent supply pipes 4a and 4b. As
20 illustrated in FIG. 2C, which is a sectional view taken along line B-B in FIG. 2A, the downstream side of the gap 13 in the flow path of the silver complex solution is connected to a slit portion 12 having an opening 11 facing radially outward along the inner periphery of the pipe 2. As illustrated in FIG. 2B, which is a sectional view taken along line A-A in FIG. 2A, when the reducing
25 agent is introduced into the gap 13 from the interiors of the reducing agent supply pipes 4a and 4b, the reducing agent reaches the slit portion 12 through the gap 13, and enters the pipe 2 through the opening 11 of the slit portion 12 from the entire circumference of the pipe 2 substantially perpendicularly (for example, at an angle of 75 degrees or more and 105 degrees or less). The
30 reducing agent is thus added to the silver complex solution. Here, the angle at which the reducing agent enters the flow path of the silver complex solution is the angle between the axial direction of the pipe 2 and the opening direction of the opening 11 through which the reducing agent enters the pipe 2. The opening direction can be regarded as the direction along the wall surface near the
35 opening of the slit portion 12, as illustrated in FIG. 2B.

[0079] The flow velocity of the reducing agent when added to the flow path of

the silver complex solution can be controlled based on the flow rate of the reducing agent supplied to the reducing agent supply pipes 4a and 4b and the total area of the opening 11. By controlling the flow velocity of the reducing agent within the foregoing range, the reaction between the silver complex and the reducing agent can be carried out quickly, so that silver powder having a sharp particle size distribution can be obtained.

[0080] The width of the opening 11 of the slit portion 12 in FIGS. 2B and 2C is referred to as "slit width". The slit width is preferably narrower than the diameter of the reducing agent supply pipe in order to reduce the total area of the opening 11. The shapes of the gap 13 and the slit portion 12, which allow the reducing agent to be added to the flow path from a plurality of directions and allow formation of a slit width narrower than the diameter of the reducing agent supply pipe, are not limited to the structures illustrated in FIGS. 2A to 2C, and various modifications are possible. For example, instead of providing the opening 11 over the entire circumference of the pipe 2, a plurality of through-holes may be provided.

[0081] The number of reducing agent supply pipes for supplying the reducing agent into the reducing agent addition member 10 is one or more, and preferably two or more. If there are two or more reducing agent supply pipes, the flow paths of the reducing agent from the reducing agent supply pipes to the opening 11 may be opposed or eccentric. In FIGS. 2A to 2C, the reducing agent supply pipes 4a and 4b are connected eccentrically with respect to the center of the pipe 2, and the flow paths of the reducing agent supply pipes 4a and 4b are connected to the slit portion 12 having the opening 11. When connecting a plurality of reducing agent supply pipes, at least two reducing agent supply pipes may be eccentrically arranged. In this way, the reducing agent can be caused to flow into the opening 11 of the slit portion 12 while being rotated in one direction along the outer periphery of the silver complex solution flow path (pipe 2).

When the reducing agent is rotated along the outer periphery of the silver complex solution flow path, the flow rate of the reducing agent toward the opening 11 may be adjusted by changing the cross-sectional area of the reducing agent flow path (the gap 13 or the slit portion 12).

[0082] (Resin-curable Conductive Paste)

A resin-curable conductive paste according to the present disclosure contains the above-described silver powder according to the present disclosure.

The proportion of the silver powder according to the present disclosure in the total amount of metal powder contained in the resin-curable conductive paste is 20 % to 100 %. The resin-curable conductive paste according to the present disclosure preferably contains silver powder having a particle diameter (D_{50}) larger than that of the silver powder according to the present disclosure, as metal powder other than the silver powder according to the present disclosure. As a result of containing the silver powder according to the present disclosure, the resin-curable conductive paste according to the present disclosure has low volume resistivity even when fired at low temperatures.

10 The resin-curable conductive paste according to the present disclosure typically contains the silver powder according to the present disclosure, a resin, and a solvent. The resin-curable conductive paste according to the present disclosure may optionally further contain components other than the silver powder, resin, and solvent (hereinafter also referred to as “other components”).

15 **[0083]** The resin is not limited, and examples thereof include silicone resin, epoxy resin, acrylic resin, polyester resin, polyimide resin, polyurethane resin, phenoxy resin, and cellulose-based resin (ethyl cellulose, hydroxypropyl cellulose, etc.). These may be used alone or in combination of two or more in any ratio.

20 **[0084]** The solvent is not particularly limited, and examples thereof include alcohol-based solvents such as terpineol, butyl carbitol, texanol, ethylene glycol, diethylene glycol, and glycerin; ester-based solvents such as butyl carbitol acetate and ethyl acetate; and hydrocarbon-based solvents such as toluene, xylene, and cyclohexane. These may be used alone or in combination of two or more in any ratio.

[0085] Examples of the other components include dispersants, surfactants, viscosity modifiers, and slip agents.

30 **[0086]** The method of producing the resin-curable conductive paste is not particularly limited, and a method of mixing the silver powder according to the present disclosure, an organic binder, a solvent, and optionally other components may be used. The mixing method is not particularly limited, and a planetary stirrer, ultrasonic dispersion, a disper, a three-roll mill, a ball mill, a bead mill, a two-axis kneader, etc. may be used.

35 **[0087]** The resin-curable conductive paste according to the present disclosure may be applied to a substrate by, for example, printing such as screen printing, offset printing, or photolithography, or dipping to form a coating film. The

coating film may be formed into a predetermined pattern by photolithography using a resist.

[0088] The coating film may be heated and cured to form a conductive film. The heat curing may be performed in an air atmosphere or in a non-oxidizing atmosphere such as nitrogen.

[0089] The resin-curable conductive paste according to the present disclosure has low volume resistivity even when fired at low temperatures, and therefore is suitable for use in the production of heterojunction (HJT) type solar cells and the like, where electrodes and conductor patterns are formed by heating at relatively low temperatures.

EXAMPLES

[0090] The present disclosure will be described in more detail below by way of examples; however, the present disclosure is not limited in any way to the following examples.

The BET specific surface area, true density, average primary particle diameter D_{SEM} , particle size distribution, ignition loss (Ig-loss) value, quantity of surface treatment agent, oxygen content and carbon content of silver powder, surface treatment agent-derived carbon content, and crystallite diameter were measured or calculated by the methods described above.

[0091] (Example 1)

Silver powder was produced using the silver powder production device 1 illustrated in FIGS. 1 and 2A to 2C.

A 0.160 mol/L silver nitrate aqueous solution was introduced into the pipe 2 (inner diameter: 20 mm) at a liquid temperature of 50 °C and a flow rate of 23.35 L/min. A 0.024 mol/L nitric acid aqueous solution was introduced from the pH adjuster supply pipe 7 (inner diameter: 6 mm), which is a coaxial double pipe, at a flow rate of 2.13 L/min to adjust the pH. 4.500 mol/L ammonia water as a complexing agent was introduced from the complexing agent supply pipe 6 (inner diameter: 6 mm), which is a coaxial double pipe, at a flow rate of 2.33 L/min to generate a silver ammine complex within the pipe 2.

A surface treatment agent (0.10 mass% Celozole 920 (produced by Chukyo Yushi Co., Ltd., containing 15.5 wt% stearic acid)) was introduced from the surface treatment agent supply pipe 5 (inner diameter: 6 mm) upstream of the reducing agent addition member 10, at a flow rate of 2.19 L/min. The amount of the silver nitrate aqueous solution was such that the

silver concentration in the total solution after adding the pH adjuster, complexing agent, reducing agent, and surface treatment agent was 0.115 mol/L.

5 A 0.500 mol/L hydrazine aqueous solution as a reducing agent was introduced from the entire circumference of the slit portion 12 (slit width: 0.44 mm, pipe inner diameter: 20.6 mm) of the reducing agent addition member 10 at a flow rate of 2.55 L/min, to precipitate silver powder. The flow velocity of the reducing agent entering through the slit portion having a slit width of 0.44 mm was 1.49 m/sec. The flow velocity of the silver ammine complex
10 immediately before the addition of the reducing agent at the pipe 2 inner diameter of 20.6 mm at the reducing agent entrance position was 1.50 m/sec. The ratio of the flow velocity of the complex to the flow velocity of the reducing agent (complex flow velocity/reducing agent flow velocity) was 1.01.

The operating time of the silver powder production device (i.e., the
15 time from the start to the stop of introduction of the reducing agent to the silver ammine complex after the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized) was 616 seconds. The slurry generated before the flow of the silver ammine complex stabilized was collected in a separate container and separated from the silver powder
20 according to the present disclosure.

In the above, the time from the inlet of the flow path of the silver nitrate aqueous solution to the nitric acid aqueous solution addition position was 0.5 seconds, the time from the nitric acid aqueous solution addition position to the ammonia water addition position was 0.5 seconds, the time from the ammonia
25 water addition position to the hydrazine aqueous solution addition position was 2.12 seconds (2.1 m), and the time from the surface treatment agent addition position to the hydrazine aqueous solution addition position was 0.12 seconds. The temperature of the silver ammine complex aqueous solution immediately before the hydrazine aqueous solution addition position was 47.2 °C.

30 **[0092]** The silver powder-containing slurry was discharged from the pipe 2. The time from the hydrazine aqueous solution addition position to the discharge was approximately 2 seconds. After the reduction reaction had stabilized, the silver powder-containing slurry was collected, and the solid obtained by solid-liquid separation was washed with pure water to remove
35 impurities contained in the solid. The endpoint of washing was determined based on the electrical conductivity of the water after washing. Washing was

continued until the electrical conductivity reached 0.5 mS/m or less. Thereafter, drying was performed to obtain 3.8 kg of silver powder.

[0093] The obtained silver powder was subjected to disintegration using a sample mill (SK-M10 produced by Kyoritsu Riko Co., Ltd.), where 120 g of the silver powder was charged and disintegrated twice for 90 seconds. As a result, the silver powder according to Example 1 was obtained.

[0094] The measurement results, etc. for the silver powder according to Example 1 are shown in Table 3. FIG. 3 is an SEM photograph (20,000x magnification) of the silver powder according to Example 1.

10 [0095] (Examples 2 and 3)

Silver powders according to Examples 2 and 3 were produced in the same manner as in Example 1, except that the conditions were changed as shown in Tables 1 and 2. The measurement results, etc. for the silver powders according to Examples 2 and 3 are shown in Table 3. FIGS. 4 and 5 are SEM photographs (20,000x magnification) of the silver powders according to Examples 2 and 3.

[0096] (Example 4)

A 0.070 mol/L silver nitrate aqueous solution was introduced into the pipe 2 (inner diameter: 20 mm) at a liquid temperature of 50 °C and a flow rate of 23.35 L/min. A 0.016 mol/L sodium carbonate aqueous solution was introduced from the pH adjuster supply pipe 7 (inner diameter: 6 mm), which is a coaxial double pipe, at a flow rate of 2.13 L/min to adjust the pH. 3.773 mol/L ammonia water as a complexing agent was introduced from the complexing agent supply pipe 6 (inner diameter: 6 mm), which is a coaxial double pipe, at a flow rate of 2.33 L/min to generate a silver ammine complex within the pipe 2.

A 0.08 mass% surface treatment agent (Celozole 920 (produced by Chukyo Yushi Co., Ltd., containing 15.5 wt% stearic acid)) was introduced from the surface treatment agent supply pipe 5 (inner diameter: 6 mm) upstream of the reducing agent addition member 10, at a flow rate of 2.19 L/min. The amount of the silver nitrate aqueous solution was such that the silver concentration in the total solution after adding the pH adjuster, complexing agent, reducing agent, and surface treatment agent was 0.050 mol/L.

35 A 0.240 mol/L aqueous hydrazine carbonate solution as a reducing agent was introduced from the entire circumference of the slit portion 12 (slit

width: 0.44 mm, pipe inner diameter: 20.6 mm) of the reducing agent addition member 10 at a flow rate of 2.55 L/min, to precipitate silver powder. The flow velocity of the reducing agent entering through the slit portion having a slit width of 0.44 mm was 1.49 m/sec. The flow velocity of the silver ammine complex immediately before the addition of the reducing agent at the pipe 2 inner diameter of 20.6 mm at the reducing agent entrance position was 1.50 m/sec. The ratio of the flow velocity of the complex to the flow velocity of the reducing agent (complex flow velocity/reducing agent flow velocity) was 1.01.

The operating time of the silver powder production device (i.e., the time from the start to the stop of introduction of the reducing agent to the silver ammine complex after the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized) was 83 seconds. The slurry generated before the flow of the silver ammine complex stabilized was collected in a separate container and separated from the silver powder according to the present disclosure.

In the above, the time from the inlet of the flow path of the silver nitrate aqueous solution to the sodium carbonate aqueous solution addition position was 0.5 seconds, the time from the sodium carbonate aqueous solution addition position to the ammonia water addition position was 0.5 seconds, the time from the ammonia water addition position to the hydrazine carbonate aqueous solution addition position was 2.12 seconds (2.1 m), and the time from the surface treatment agent addition position to the hydrazine carbonate aqueous solution addition position was 0.12 seconds. The temperature of the silver ammine complex aqueous solution immediately before the hydrazine carbonate aqueous solution addition position was 46.5 °C.

[0097] The silver powder-containing slurry was discharged from the pipe 2. The time from the hydrazine carbonate aqueous solution addition position to the discharge was approximately 2 seconds. After the reduction reaction had stabilized, the silver powder-containing slurry was collected, and the solid obtained by solid-liquid separation was washed with pure water to remove impurities contained in the solid. The endpoint of washing was determined based on the electrical conductivity of the water after washing. Washing was continued until the electrical conductivity reached 0.5 mS/m or less. After drying, 0.24 kg of silver powder was obtained.

[0098] The silver powder obtained in Example 4 was subjected to the same pulverization treatment as in Example 1.

The measurement results, etc. for the silver powder according to Example 4 are shown in Table 3. FIG. 6 is an SEM photograph (20,000x magnification) of the silver powder according to Example 4.

[0099] (Comparative Example 1)

5 124.65 g of industrial ammonia water having a concentration of 28 mass% was added to 3,233.4 g of a silver nitrate aqueous solution containing 40.99 g (0.38 mol) of silver (corresponding to 5.4 mol equivalents of ammonia per 1 mol of silver) to obtain a silver ammine complex aqueous solution.

 2.28 g of a sodium hydroxide aqueous solution having a concentration
10 of 20 mass% was added to the silver ammine complex aqueous solution, and the liquid temperature was adjusted to 25 °C. After this, 111.17 g of a hydrazine aqueous solution having a concentration of 7.3 mass% was added while stirring, to obtain a slurry containing silver particles. Further, 12.69 g of a 1.55 mass%
15 stearic acid emulsion was added to the obtained slurry containing silver particles and stirred. Thereafter, stirring was stopped to allow the silver particles to settle, and the liquid in which the silver particles had precipitated was filtered. The filtrate was washed with water until the electrical conductivity of the filtrate after washing would be 0.5 mS/m or less, and then vacuum-dried at 73 °C.

20 **[0100]** The foregoing silver powder production was repeatedly performed three times to obtain silver powder. The obtained silver powder was subjected to disintegration using a sample mill (SK-M10 produced by Kyoritsu Riko Co., Ltd.), where 120 g of silver was charged and disintegrated twice for 90 seconds. As a result, the silver powder according to Comparative Example 1 was
25 obtained.

[0101] The measurement results, etc. for the silver powder according to Comparative Example 1 are shown in Table 3. FIG. 7 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 1.

30 **[0102]** (Comparative Example 2)

 3.3 g of a 60 mass% nitric acid aqueous solution was added to 3,374.7 g of a silver nitrate aqueous solution containing 45.32 g (0.42 mol) of silver, and further 76.5 g of industrial ammonia water having a concentration of 28 mass% (corresponding to 3 mol equivalents of ammonia per 1 mol of silver)
35 was added to obtain a silver ammine complex aqueous solution.

 The liquid temperature of the silver ammine complex aqueous solution

was adjusted to 35 °C. After this, 20.57 g of a 1.1 mass% sodium benzotriazole aqueous solution was added as an azole compound (corresponding to addition of sodium benzotriazole in an amount of 0.5 mass% relative to silver) to obtain a first liquid. 142.7 g of an aqueous hydrazine hydrate solution having a
5 concentration of 5.6 mass% was then added as a reducing agent to the first liquid, to obtain a second liquid as a slurry containing fine silver particles. Further, 17.54 g of a 1.55 mass% stearic acid emulsion was added to the second liquid and stirred. Thereafter, stirring was stopped to allow the silver particles to settle, and the liquid in which the silver particles had precipitated was
10 filtered. The filtrate was washed with water until the electrical conductivity of the filtrate after washing would be 0.5 mS/m or less, and then vacuum-dried at 73 °C.

[0103] The foregoing silver powder production was repeatedly performed three times to obtain silver powder. The obtained silver powder was subjected
15 to disintegration using a sample mill (SK-M10 produced by Kyoritsu Riko Co., Ltd.), where 120 g of the silver powder was charged and disintegrated twice for 90 seconds. As a result, the silver powder according to Comparative Example 2 was obtained.

[0104] The measurement results, etc. for the silver powder according to
20 Comparative Example 2 are shown in Table 3. FIG. 8 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 2.

		Production method	Silver nitrate aqueous solution (silver-containing solution)		pH adjuster			Ammonia water (complexing agent)		Stearic acid (surface treatment agent)		Reducing agent		
			Concentration [mol/L]	Flow rate [L/min]	Type	Concentration [mol/L]	Flow rate [L/min]	Concentration [mol/L]	Flow rate [L/min]	Concentration [wt%]	Flow rate [L/min]	Type	Concentration [mol/L]	Flow rate [L/min]
Example	1	Continuous	0.160	23.35	Nitric acid	0.024	2.13	4.500	2.33	0.0155	2.19	Hydrazine	0.500	2.55
	2	Continuous	0.153	23.35	Nitric acid	0.024	2.13	4.436	2.33	0.0155	2.19	Hydrazine	0.500	2.55
	3	Continuous	0.160	27.24	Nitric acid	0.024	2.49	4.436	2.72	0.0155	2.55	Hydrazine	0.500	2.97
	4	Continuous	0.070	23.35	Sodium carbonate	0.016	2.13	3.773	2.33	0.0804	2.19	Hydrazine carbonate	0.240	2.55
Comparative Example	1	Batch	-	-	-	-	-	-	-	-	-	-	-	-
	2	Batch	-	-	-	-	-	-	-	-	-	-	-	-

[0105] [Table 1]

		Production method	Silver concentration in total solution after adding pH adjuster, complexing agent, reducing agent, and surface treatment agent [mol/L]	Complex flow velocity [m/sec]	Reducing agent flow velocity [m/sec]	Complex flow velocity/ reducing agent flow velocity	Operating time [sec]	Obtained silver powder [kg]
Example	1	Continuous	0.115	1.50	1.49	1.01	616	3.8
	2	Continuous	0.115	1.50	1.49	1.01	617	3.6
	3	Continuous	0.115	1.75	1.74	1.01	568	3.2
	4	Continuous	0.050	1.50	1.49	1.01	83	0.24
Comparative Example	1	Batch	-	-	-	-	-	-
	2	Batch	-	-	-	-	-	-

[0106] [Table 2]

		BET specific surface area [m ² /g]	Crystallite diameter	True density [g/cm ³]	D _{SEM} [μm]	Particle size distribution			Ig-loss [%]	Ig-loss /BET specific surface area	Oxygen content of silver powder [mass%]	Oxygen content of silver powder /BET specific surface area	Carbon content of silver powder [mass%]	Content of surface treatment agent [mass%]
			Dx [nm]			D ₁₀ [μm]	D ₅₀ [μm]	D ₉₀ [μm]						
Example	1	1.16	38	9.99	0.45	0.22	0.57	0.99	0.62	0.53	0.130	0.112	0.420	0.48
	2	1.12	34	10.01	0.51	0.24	0.63	0.92	0.58	0.52	0.140	0.125	0.390	0.47
	3	1.17	35	9.97	0.59	0.26	0.62	1.04	0.63	0.54	0.140	0.120	0.440	0.52
	4	1.72	30	9.84	0.23	0.13	0.31	0.65	0.93	0.54	0.200	0.120	0.630	0.71
Comparative Example	1	1.04	45	10.07	0.51	0.313	0.83	1.50	0.52	0.50	0.110	0.106	0.370	0.44
	2	1.78	38	9.93	0.40	0.153	0.47	0.93	0.71	0.40	0.160	0.090	0.490	0.54

[0107] [Table 3]

[0108] (Paste Evaluation)

<Volume Resistivity>

First, resin-curable conductive pastes were prepared using the silver powders obtained in Examples 1 and 4 and Comparative Examples 1 and 2. Specifically, the silver powder to be evaluated and AG-5-54F produced by DOWA Electronics Materials Co., Ltd. (D_{50} : 2.9 μm , BET: 0.21 m^2/g , TAP: 6.1 g/cm^3) as a filler were mixed in a mass ratio of 5:5 to obtain a mixed silver powder. Then, 91.92 parts by mass of the mixed silver powder, 3.87 parts by mass of a first epoxy resin (EP4901E produced by ADEKA Corporation), 0.97 parts by mass of a second epoxy resin (JER1009 produced by Mitsubishi Chemical Corporation), 0.24 parts by mass of a curing agent (boron trifluoride monoethylamine complex produced by FUJIFILM Wako Pure Chemical Corporation), and 3.00 parts by mass of a solvent (BCA: butyl carbitol acetate) were taken out and placed in a propeller-less planetary stirring and defoaming device (VMX-N360 produced by EME Corporation), and mixed by stirring at 1200 rpm for 30 seconds. The mixture was then passed through a three-roll mill (80S produced by Exakt Technologies Inc.) with a roll gap of 100 μm to 20 μm to be kneaded, thereby obtaining a resin-curable conductive paste before viscosity adjustment. Further, a required amount of BCA was added to the resin-curable conductive paste before viscosity adjustment to obtain a conductive paste after viscosity adjustment having a viscosity adjusted to 300 Pa·s. The viscosity adjustment of the resin-curable conductive paste was carried out by gradually adding BCA in small portions to the resin-curable conductive paste before viscosity adjustment while sequentially measuring the viscosity.

Using the obtained resin-curable conductive paste, ten lines were formed for each of line widths (design widths) of 15 μm and 19 μm using a screen printing plate (#480 mesh), as evaluation targets. The squeegee speed during printing was 350 mm/sec, and printing was performed twice.

The printed patterns were then dried at 150 °C for 10 minutes using an air-circulating dryer, and further cured by heating at 200 °C for 30 minutes to form line-shaped conductive films (wiring). For the obtained conductive films, the volume resistivity was measured.

Measurement terminals were placed at both ends of each conductive film, and the line resistance (Ω) was measured using a digital multimeter (produced by ADC Corporation). The line resistance value was taken as the

average value of 20 line patterns (ten lines printed twice), excluding those regarded as disconnections as described below. Line patterns showing an extremely high measured resistance of 100 k Ω or more during line resistance measurement were regarded as disconnections. In addition, the shape of the wiring in the line width direction was measured at ten locations (five locations printed twice) using a laser microscope (VK-X1000 produced by KEYENCE Corporation), and the average value of the cross-sectional area of the wiring was calculated.

From the measured line resistance and the above cross-sectional area, the volume resistivity was calculated using the following formula (1):

$$\text{Volume resistivity } [\Omega \cdot \text{cm}] = \text{Line resistance } [\Omega] \times \text{Cross-sectional area } [\text{cm}^2] / \text{Line length } [\text{cm}] \quad (1).$$

The line length (design length) used in measuring line resistance was 150 mm. The measurement results of the volume resistivity are shown in Table 4.

[0109] [Table 4]

	Volume resistivity [$\Omega \cdot \text{cm}$]	
Line width	15 μm	19 μm
Example 1	7.7	7.8
Example 4	7.3	7.2
Comparative Example 1	8.4	8.0
Comparative Example 2	8.1	8.7

[0110] As is clear from Table 4, silver powders containing a surface treatment agent and having a ratio of oxygen content to BET specific surface area of 0.11 or more and a crystallite diameter of 30 nm or more and 38 nm or less are capable of, in the case of being formed into a conductive paste, imparting low volume resistivity even when fired at low temperatures.

INDUSTRIAL APPLICABILITY

[0111] It is thus possible to provide a silver powder capable of, in the case of being formed into a conductive paste, imparting low volume resistivity even when fired at low temperatures.

It is also possible to provide a resin-curable conductive paste capable of achieving low volume resistivity even when fired at low temperatures.

REFERENCE SIGNS LIST

5	[0112] 1	silver powder production device
	2	pipe
	4a	reducing agent supply pipe
	4b	reducing agent supply pipe
	5	surface treatment agent supply pipe
10	6	complexing agent supply pipe
	7	pH adjuster supply pipe
	10	reducing agent addition member
	11	opening
	12	slit portion
	13	gap

CLAIMS

- [Claim 1] A silver powder comprising:
a surface treatment agent;
5 a ratio of oxygen content to BET specific surface area of 0.11 or more;
and
a crystallite diameter of 30 nm or more and 38 nm or less.
- [Claim 2] The silver powder according to claim 1, comprising a ratio of
10 Ig-loss to the BET specific surface area of 0.51 or more.
- [Claim 3] The silver powder according to claim 1, comprising:
a volume-based cumulative 50 % diameter D_{50} measured by a laser
diffraction method of 0.1 μm or more and 1.0 μm or less; and
15 a volume-based cumulative 90 % diameter D_{90} measured by the laser
diffraction method of 1.2 μm or less.
- [Claim 4] The silver powder according to claim 1, wherein the BET
specific surface area is 0.90 m^2/g or more and 2.50 m^2/g or less.
20
- [Claim 5] The silver powder according to any one of claims 1 to 4, for
use in a resin-curable conductive paste.
- [Claim 6] A resin-curable conductive paste comprising the silver powder
25 according to any one of claims 1 to 4.