

DESCRIPTION

TITLE

SILVER POWDER, SILVER POWDER PRODUCTION METHOD, SILVER
5 POWDER PRODUCTION DEVICE, AND RESIN-CURABLE CONDUCTIVE
PASTE

TECHNICAL FIELD

[0001] The present disclosure relates to a silver powder, a silver powder
10 production method, a silver powder production device, and a resin-curable
conductive paste.

BACKGROUND

[0002] Conventionally, conductive pastes prepared by blending metal powders
15 such as silver powder with solvents, resins, dispersants, and the like have been
used to form electrodes and wiring of electronic components by printing
methods or the like.

[0003] In recent years, heterojunction (HJT) type solar cells have attracted
attention. In HJT type solar cells and the like, electrodes and conductor patterns
20 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.

[0004] For example, JP 2013-159805 A (PTL 1) proposes fine silver particles
obtained by a predetermined production method and having an average particle
25 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.

CITATION LIST

30 Patent Literature

[0005] PTL 1: JP 2013-159805 A

SUMMARY

(Technical Problem)

35 [0006] When the firing temperature for forming electrodes, conductor patterns,
etc. is lowered to, for example, 150 °C to 200 °C, a problem of increased

volume resistivity may arise. It is desirable to suppress an increase in the volume resistivity of a conductive paste containing silver powder even when the firing temperature is lowered.

5 **[0007]** In recent years, electrodes, conductor patterns, etc. have been increasingly made finer. Accordingly, when a conductive paste containing silver powder is used to form electrodes, conductor patterns, etc., it is desirable that the conductive paste exhibits excellent fine-line printability, that is, even if printing is performed with a finer line width than conventional ones, line breakage is unlikely to occur and disconnection after firing is unlikely to occur.

10 **[0008]** It could therefore be helpful to provide a silver powder capable of, in the case of being formed into a conductive paste, imparting excellent volume resistivity and fine-line printability even when fired at low temperatures, and a production method therefor.

15 It could also be helpful to provide a silver powder production device capable of producing the silver powder.

It could further be helpful to provide a resin-curable conductive paste having excellent volume resistivity and fine-line printability even when fired at low temperatures.

(Solution to Problem)

20 **[0009]** Intensive studies made to achieve the objects stated above led to the present disclosure.

[0010] We thus provide the following.

[0011] [1] A silver powder 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; a ratio of D_{50} to BET diameter D_{BET} of 1.3 or less; and a shrinkage ratio at 200 °C in thermomechanical analysis of 1 % or more.

[0012] [2] The silver powder according to [1], comprising a shrinkage ratio at 150 °C in thermomechanical analysis of 0.6 % or more.

30 **[0013]** [3] The silver powder according to [1] or [2], comprising a BET specific surface area of 0.90 m^2/g or more and 2.50 m^2/g or less.

[0014] [4] The silver powder according to any one of [1] to [3], for use in a resin-curable conductive paste.

35 **[0015]** [5] A silver powder production method comprising: flowing a 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 a hydrazine-based reducing agent to the flow path at a reducing agent addition position downstream of the complexing agent addition position; and reducing and precipitating silver powder in the flow path.

5 **[0016]** [6] The silver powder production method according to [5], wherein a time required for the silver-containing solution to flow from the complexing agent addition position to the reducing agent addition position is 0.1 seconds or more and 10 seconds or less.

10 **[0017]** [7] The silver powder production method according to [5] or [6], comprising adding a surface treatment agent to the flow path between the complexing agent addition position and the reducing agent addition position, or downstream of the reducing agent addition position.

15 **[0018]** [8] A silver powder production device that adds a pH adjuster, a complexing agent, and a hydrazine-based reducing agent as a reducing agent to a silver-containing solution to reduce and precipitate silver powder, the silver powder production device comprising: a pipe forming a flow path of the silver-containing solution; a pH adjuster addition portion connected to the pipe; a complexing agent addition portion; and a reducing agent addition portion connected to the pipe downstream of the nitric acid addition portion and the complexing agent addition portion.

20 **[0019]** [9] A resin-curable conductive paste comprising the silver powder according to any one of [1] to [3].

(Advantageous Effect)

25 **[0020]** It is thus possible to provide a silver powder capable of, in the case of being formed into a conductive paste, imparting excellent volume resistivity and fine-line printability even when fired at low temperatures, a production method for the silver powder, a silver powder production device capable of producing the silver powder, and a resin-curable conductive paste having excellent volume resistivity and fine-line printability even when fired at low
30 temperatures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] In the accompanying drawings:

35 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;

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;

5 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 a graph illustrating the results of thermomechanical analysis of the silver powders obtained in Examples 1 to 8 and Comparative Examples 1 and 2;

10 FIG. 4 is a graph illustrating an enlarged part of the graph in FIG. 3;

FIG. 5 is an SEM photograph (20,000x magnification) of the silver powder according to Example 1;

FIG. 6 is an SEM photograph (20,000x magnification) of the silver powder according to Example 2;

15 FIG. 7 is an SEM photograph (20,000x magnification) of the silver powder according to Example 3;

FIG. 8 is an SEM photograph (20,000x magnification) of the silver powder according to Example 4;

20 FIG. 9 is an SEM photograph (20,000x magnification) of the silver powder according to Example 5;

FIG. 10 is an SEM photograph (20,000x magnification) of the silver powder according to Example 6;

FIG. 11 is an SEM photograph (20,000x magnification) of the silver powder according to Example 7;

25 FIG. 12 is an SEM photograph (20,000x magnification) of the silver powder according to Example 8;

FIG. 13 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 1; and

30 FIG. 14 is an SEM photograph (20,000x magnification) of the silver powder according to Comparative Example 2.

DETAILED DESCRIPTION

[0022] (Terminology and Measurement Methods)

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

[0023] <Shrinkage Ratio of Silver Powder>

The shrinkage ratio of silver powder was measured as follows.

First, 0.3 g of silver powder was weighed. Next, the silver powder was placed in a predetermined mold having a diameter of 5 mm ϕ , and compressed using a press machine under a load of 50 kg for 1 minute to prepare a cylindrical measurement sample. This measurement sample was set in a sample holder of a thermomechanical analysis (TMA) device (Thermo plus EVO 2 series TMA8311). While applying a measurement load of 98 mN using a measurement probe, the temperature was increased from room temperature (25 °C $\pm$ 5) to 900 °C at a heating rate of 10 °C/min to perform thermomechanical analysis (TMA) of the measurement sample. The shrinkage ratio at 200 °C in thermomechanical analysis and the shrinkage ratio at 150 °C in thermomechanical analysis were calculated using the following formulas (1) and (2), respectively:

$$\text{Shrinkage ratio at 200 } ^\circ\text{C in thermomechanical analysis (\%)} = (L_{\text{RT}} - L_{200})/L_{\text{RT}} \times 100 \quad (1)$$

$$\text{Shrinkage ratio at 150 } ^\circ\text{C in thermomechanical analysis (\%)} = (L_{\text{RT}} - L_{150})/L_{\text{RT}} \times 100 \quad (2)$$

where L_{RT} is the axial length (mm) of the cylindrical measurement sample at room temperature (25 °C $\pm$ 5), L_{200} is the axial length (mm) of the cylindrical measurement sample at a temperature of 200 °C, and L_{150} is the axial length (mm) of the cylindrical measurement sample at a temperature of 150 °C.

[0024] <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.

[0025] <True Density Measurement>

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.

[0026] <BET Diameter D_{BET} >

The BET diameter D_{BET} (hereinafter also simply referred to as “ D_{BET} ”) (unit: μm) is the particle diameter converted from the BET specific surface area (unit: m^2/g) measured by the single-point BET method and the true density (unit: g/cm^3), and was calculated using the following formula (3):

$$D_{\text{BET}} = 6/(\text{BET specific surface area} \times \text{True density}) \quad (3).$$

[0027] <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.).

[0028] <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.

[0029] <Ratio of D_{50} to D_{BET} (D_{50}/D_{BET})>

Silver powder particles may not be completely separated from one another, and may instead form agglomerates. In particle diameter measurement by the laser diffraction method, the particle diameter of agglomerated particles is measured in the agglomerated state. On the other hand, the single-point BET

method measures the specific surface area using the amount of gas adsorbed onto particles, and the BET diameter converted from this specific surface area represents the particle diameter of the particle assuming that the measured particle is a true sphere. If there is little agglomeration and the particle is close to monodisperse, the ratio (D_{50}/D_{BET}) tends to be close to 1.

[0030] <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. 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 using the following formula: Ignition loss (Ig-loss) value (mass%) = $(w_1 - w_2)/w_1 \times 100$.

[0031] <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, the content of the fatty acid was measured according to the fatty acid quantitative analysis 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 solvent was evaporated to dryness. The remaining solid (the surface treatment agent that solidified without evaporating) 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.

[0032] For example, if the surface treatment agent is identified as stearic acid and no carbon sources other than stearic acid are contained in the silver powder, the method of measuring the content of stearic acid is as described in the above publication.

[0033] In this specification, for example, in the case where the surface treatment agent of silver powder is benzotriazole, the content of benzotriazole was measured according to the quantitative analysis method for benzotriazole and benzotriazole salts described in JP 5523153 B2.

5 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.

[0034] The type of surface treatment agent can be identified by qualitative analysis using gas chromatography of the surface treatment agent volatilized
10 by heating the silver powder.

[0035] <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
15 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
20 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.

[0036] (Silver Powder)

 A silver powder according to the present disclosure comprises: a
25 volume-based D_{50} measured by a laser diffraction method of 0.1 μm or more and 1.0 μm or less; a ratio of D_{50} to D_{BET} (D_{50}/D_{BET}) of 1.3 or less; and a shrinkage ratio at 200 °C in thermomechanical analysis of 1 % or more.

 Such silver powder can impart excellent volume resistivity even when fired at low temperatures (150 °C to 200 °C) in a conductive paste state. The
30 reason for this is presumed to be that, as a result of silver powder with a D_{50}/D_{BET} of 1.3 or less and in a nearly monodisperse state having a shrinkage ratio of at least a predetermined level at 200 °C, silver particles are allowed to form a favorable conductive network during firing in electrodes, conductor patterns, and the like obtained using a conductive paste containing the silver
35 powder, as compared with silver powder having a lower shrinkage ratio at 200 °C. In this specification, the property of having low volume resistivity and low

disconnection rate even when fired at low temperatures (150 °C to 200 °C) is also referred to as “low-temperature firing property.”

Such silver powder can also impart excellent fine-line printability to the conductive paste. The reason for this is presumed to be that, as a result of
5 D₅₀ being within the specified range, deterioration of fine-line printability due to large particle diameter and excessive increase in the viscosity of the conductive paste containing the silver powder can be effectively suppressed.

[0037] The shrinkage ratio at 200 °C in thermomechanical analysis is 1.0 % or more, preferably 1.1 % or more, and more preferably 1.3 % or more.

10 If the shrinkage ratio at 200 °C in thermomechanical analysis is 1.0 % or more, low-temperature firing property can be improved.

Since D₅₀/D_{BET} is 1.3 or less, the shrinkage ratio does not exceed 5.0 %. The shrinkage ratio at 200 °C in thermomechanical analysis is, for example, preferably 5.0 % or less, and more preferably 3.0 % or less.

15 **[0038]** The shrinkage ratio at 150 °C in thermomechanical analysis is preferably 0.6 % or more, more preferably 0.7 % or more, and further preferably 0.8 % or more.

If the shrinkage ratio at 150 °C in thermomechanical analysis is 0.6 % or more, the low-temperature firing property can be achieved more effectively.

20 The shrinkage ratio at 150 °C in thermomechanical analysis is, for example, preferably 3.0 % or less, more preferably 1.5 % or less, and further preferably 1.3 % or less. 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
25 disclosure, the shrinkage ratio at 150 °C in thermomechanical analysis according to the present disclosure may be 1.05 % or more and 1.5 % or less, and may be 1.05 % or more and 1.4 % or less.

[0039] D₅₀/D_{BET} is preferably 1.3 or less, more preferably 1.27 or less, and further preferably 1.20 or less.

30 If D₅₀/D_{BET} is 1.3 or less, excellent dispersibility can be obtained, and thus excellent fine-line printability can be imparted.

Although D₅₀/D_{BET} is often 1.0 or more, D₅₀/D_{BET} may be less than 1.0 as in Examples. In such a case, D₅₀/D_{BET} is preferably 0.8 or more.

[0040] D₅₀ is 0.1 μm or more, preferably 0.2 μm or more, more preferably 0.25
35 μm or more, and further preferably 0.35 μm or more. D₅₀ is 1.0 μm or less, preferably 0.9 μm or less, and more preferably 0.8 μm or less. If D₅₀ is within

the above range, 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,

5 D₅₀ of the silver powder according to the present disclosure may be 0.1 μm or more and 0.5 μm or less, and may be 0.2 μm or more and 0.4 μm or less.

[0041] D₁₀ is preferably 0.05 μm or more, and more preferably 0.10 μm or more. D₁₀ is preferably 0.40 μm or less, and more preferably 0.35 μm or less.

If D₁₀ is within the above range, the fine-line printability of the
10 conductive paste can be improved.

[0042] D₉₀ is preferably 0.5 μm or more, more preferably 0.55 μm or more, and further preferably 0.6 μm or more. D₉₀ is preferably 1.2 μm or less, more preferably 1.1 μm or less, and further preferably 1.0 μm or less. If D₉₀ is within
15 the above range, 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, D₉₀ of the silver powder according to the present disclosure may be 0.5 μm or more and 0.9 μm or less, and may be 0.55 μm or more and 0.85 μm or less.

20 **[0043]** D_{BET} is preferably 0.22 μm or more, more preferably 0.25 μm or more, further preferably 0.28 μm or more, and particularly preferably 0.30 μm or more. D_{BET} is preferably 0.68 μm or less, more preferably 0.61 μm or less, and further preferably 0.58 μm or less.

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

[0044] The BET specific surface area is preferably 0.90 m²/g or more, more preferably 1.00 m²/g or more, and further preferably 1.05 m²/g or more. The BET specific surface area is preferably 2.50 m²/g or less, more preferably 2.25 m²/g or less, further preferably 2.00 m²/g or less, and even more preferably
30 1.80 m²/g or less. If the BET specific surface area is 0.90 m²/g or more, appropriate 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 m²/g or less is advantageous in
35 terms of ease of handling of the conductive paste formed from the silver powder. 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 specific surface area of the silver powder according to the present
disclosure may be 1.35 m²/g or more and 2.50 m²/g or less, and may be 1.40
5 m²/g or more and 2.50 m²/g or less.

[0045] The true density of silver is 10.49 g/cm³. The true density of the silver
powder according to the present disclosure is, for example, preferably 9.7
g/cm³ or more, more preferably 9.8 g/cm³ or more, and further preferably 9.9
g/cm³ or more, and preferably 10.49 g/cm³ or less. In the case where emphasis
10 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 true density of the silver powder
according to the present disclosure may be 9.7 g/cm³ or more and 9.95 g/cm³
or less, and may be 9.7 g/cm³ or more and 9.9 g/cm³ or less.

[0046] 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 improved. In the case where
20 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 0.15 μm or more and 0.35 μm or less.

[0047] 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, and further
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
30 can be improved. If the ignition loss value is 1.2 mass% or less, 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
35 of the silver powder according to the present disclosure may be 0.65 mass% or
more and 1.2 mass% or less, and may be 0.70 mass% or more and 1.2 mass%

or less.

[0048] The crystallite diameter is preferably 25 nm or more, and more preferably 30 nm or more. The crystallite diameter may be 30 nm or more, and preferably 32 nm or more. The crystallite diameter may be 32 nm or more. The
5 crystallite diameter is preferably 38 nm or less.

[0049] The silver powder according to the present disclosure preferably contains a surface treatment agent. If the silver powder contains a surface treatment agent, the dispersibility of the silver powder can be improved.

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

[0050] The silver powder according to the present disclosure preferably contains a surface treatment agent. If the silver powder contains a surface treatment agent, the dispersibility of the silver powder can be improved.

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

[0051] 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. However, given that the silver powder according to the present disclosure, in the case of being formed
20 into a conductive paste, exhibits excellent volume resistivity and fine-line printability even when fired at low temperatures, the silver powder according to the present disclosure is suitable for use in resin-curable conductive pastes.

[0052] (Silver Powder Production Method)

A silver powder production method (hereinafter also simply referred to
25 as “production method”) according to the present disclosure comprises: flowing a 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 a
30 hydrazine-based reducing agent to the flow path at a reducing agent addition position downstream of the complexing agent addition position; and reducing and precipitating silver powder in the flow path.

With such a production method according to the present disclosure, it is possible to obtain silver powder capable of imparting excellent volume
35 resistivity and fine-line printability to a conductive paste even when fired at low temperatures. The production method according to the present disclosure

enables obtainment of the above-described silver powder according to the present disclosure.

In the production method according to the present disclosure, 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 reduction precipitation of silver powder. This enables quantitative and continuous production of predetermined silver powder.

[0053] 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, silver chloride, silver formate, silver oxalate, and silver sulfate. From the viewpoint of availability, etc., a silver nitrate aqueous solution is preferred.

[0054] The silver concentration of the silver-containing solution is preferably 0.01 mol/L or more, more preferably 0.05 mol/L or more, and further preferably 0.10 mol/L or more, from an economic viewpoint.

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.

[0055] In this embodiment, the term “flow velocity” refers to a value obtained 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 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.

[0056] In the production method according to the present disclosure, 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, 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
5 appropriately adjusted depending on the particle diameter of the silver powder to be produced.

[0057] In the production method according to the present disclosure, 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
10 complex.

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

[0058] Examples of the complexing agent include ammonia, ammonium salts, citric acid, and acetic acid. Among these, ammonia is preferred. Ammonia can
15 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 complex is preferred because it can be easily reduced by hydrazine.

[0059] 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.

[0060] 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.

25 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.

[0061] 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 m/sec or more, and further preferably 1.00 m/sec or more, and preferably 3.20
30 m/sec or less, more preferably 2.70 m/sec or less, and further preferably 2.00 m/sec or less.

[0062] 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 above, taking into consideration the amount of the complexing agent relative
35 to the amount of silver required to form the complex.

[0063] In the production method according to the present disclosure, 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 precipitating silver powder.

Examples of the hydrazine-based reducing agent used in the present disclosure 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 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.

[0064] 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 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 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.

[0065] The amount of hydrazine 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 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.

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.

[0066] In the production method according to the present disclosure, 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
5 preferably 2.0 m/sec or less, from the viewpoint of suppressing agglomeration and forming monodisperse particles.

[0067] 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
10 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
15 liquid flow toward the pipe wall and preventing a reduction in mixing efficiency.

[0068] In the production method according to the present disclosure, 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
20 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
25 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
30 time is preferably 10.0 seconds or less, and more preferably 5.0 seconds or less.

[0069] In the production method according to the present disclosure, 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
35 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.

[0070] 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
5 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.

[0071] (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
10 acid, linoleic acid, arachidonic acid, and ricinoleic acid.

[0072] (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,
15 strontium, zirconium, silver, and copper.

[0073] (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
20 surfactants such as imidazolinium betaine; and nonionic surfactants such as polyoxyethylene alkyl ethers and polyoxyethylene fatty acid esters.

[0074] Examples of organic metals include acetylacetonate tributoxyzirconium, magnesium citrate, diethylzinc, dibutyltin oxide, dimethylzinc, tetra-n-butoxyzirconium, triethylindium, triethylgallium,
25 trimethylindium, trimethylgallium, monobutyltin oxide, tetraisocyanate silane, tetramethylsilane, tetramethoxysilane, monomethyltriisocyanate silane, silane coupling agents, titanate-based coupling agents, and aluminum-based coupling agents.

[0075] (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,
35 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.

[0076] (6) Protective Colloids

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

[0077] Among the surface treatment agents, (1) fatty acids are preferred, with stearic acid being particularly preferred, from the viewpoint of ease of modifying the silver particle surface. (1) Fatty acids are preferably in the form of emulsions, such as stearic acid emulsions.

10 **[0078]** In the production method according to the present disclosure, 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 viewpoint of reactivity in the reduction reaction.

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

[0079] In the production method according to the present disclosure, liquid mixing may be performed by applying helical rotation in the axial direction of the flow path using a mixer.

20 **[0080]** In the production method according to the present disclosure, silver powder can be obtained by discharging the liquid containing the reduced and precipitated silver powder (hereinafter also referred to as “silver powder-containing liquid”) out of the flow path and collecting it.

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

[0081] 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 or more and more preferably 2 seconds or more, from the viewpoint of allowing for the completion of the reduction reaction.

30 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.

[0082] By filtering and washing with water the silver powder-containing liquid
35 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 the silver powder according to the present disclosure is obtained. Drying can be accelerated by replacing the moisture in the cake with a lower alcohol or the like.

5 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-purpose mixer. The surface smoothing treatment can be carried out by mechanically causing particles to collide with each other using a high-speed
10 stirrer.

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

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

[0083] (Silver Powder Production Device)

A silver powder production device according to the present disclosure is an device that adds a pH adjuster, a complexing agent, and a hydrazine-based reducing agent as a reducing agent to a silver-containing solution to reduce and
20 precipitate silver powder, the device comprising: a pipe forming a flow path of the silver-containing solution; a pH adjuster addition portion connected to the pipe; a complexing agent addition portion; and a reducing agent addition portion connected to the pipe downstream of the nitric acid addition portion and the complexing agent addition portion. It is also preferable to provide a
25 surface treatment agent addition portion downstream of the nitric acid addition portion and the complexing agent addition portion and upstream of the reducing agent addition portion. 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 **[0084]** 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 **[0085]** Each of the pH adjuster addition portion, the complexing agent addition portion, and the surface treatment agent addition portion may be a Y-shaped conduit or a T-shaped conduit, or may have a structure in which a second pipe is connected midway through the pipe forming the flow path of the silver-containing solution such that the flow path of the silver-containing solution
15 and the flow path of the second pipe merge. Alternatively, each of the pH adjuster addition portion, the complexing agent addition portion, and the surface treatment agent addition portion may be a coaxial double-pipe conduit.

[0086] If the reducing agent is added to the flow path from one direction, it takes time for the reducing agent to reach the side opposite the addition point,
20 which may cause variations in the concentration of the reducing agent at the reducing agent addition position. Even in the case where a Y-shaped or T-shaped pipe is used to bring the silver complex solution and the reducing agent into contact and mix them at the confluence part, variations in concentration may occur for the same reason. In the case where a coaxial double pipe is used
25 to add the reducing agent at the center position of the flow path, the reducing agent is added in parallel with the flow of the silver complex solution. In such a case, it takes time for the silver complex solution and the reducing agent to mix. Moreover, in a coaxial double pipe, the flow velocity is relatively fast at the center of the pipe and relatively slow near the wall surface, which tends to
30 cause non-uniform particle growth.

[0087] The reducing agent is preferably added to the flow path from two or more directions, more preferably added to the flow path from four or more directions, and particularly preferably added to the flow path from all directions around the outer periphery of the flow path. By appropriately
35 selecting the number and shape of openings, the reducing agent can be added to the flow path from a plurality of directions.

[0088] The plurality of directions preferably form an angle of 75 degrees or more and 105 degrees or less with respect to the flow path. Adding the reducing agent to the flow path substantially perpendicularly is advantageous in that the silver complex solution and the reducing agent mix quickly. The angle with respect to the flow path is more preferably 80 degrees or more and 100 degrees or less. The phrase “with respect to the flow path” can be rephrased as “with respect to the axial direction of the pipe through which the silver complex solution flows.”

[0089] By using the silver powder production device according to the present disclosure, it is possible to obtain a silver powder capable of imparting excellent low-temperature heating property and fine-line printability to a conductive paste.

[0090] 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 along line B-B in FIG. 2A in a direction horizontal to the flow path of the silver complex solution.

[0091] 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 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 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 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 opening of the slit portion 12, as illustrated in FIG. 2B.

[0092] 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.

[0093] 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.

[0094] 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).

[0095] (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
5 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.
10 As a result of containing the silver powder according to the present disclosure, the resin-curable conductive paste according to the present disclosure has excellent volume resistivity and fine-line printability.

The resin-curable conductive paste according to the present disclosure typically contains the silver powder according to the present disclosure, a resin,
15 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”).

[0096] The resin is not particularly limited, and examples thereof include epoxy resin, acrylic resin, polyester resin, polyimide resin, polyurethane resin,
20 phenoxy resin, silicone resin, and ethyl cellulose. These may be used alone or in combination of two or more in any ratio.

[0097] 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
25 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.

[0098] Examples of the other components include dispersants, surfactants, viscosity modifiers, and slip agents.

[0099] 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
35 bead mill, a two-axis kneader, etc. may be used.

[0100] 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.

5 **[0101]** 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.

[0102] The resin-curable conductive paste according to the present disclosure has excellent volume resistivity and fine-line printability even when fired at
10 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

15 **[0103]** 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, BET diameter D_{BET} , average primary particle diameter D_{SEM} , particle size distribution, ignition loss
20 (Ig-loss) value, quantity of surface treatment agent, crystallite diameter, and silver powder shrinkage ratio (200 °C and 150 °C) were measured or calculated by the methods described above.

[0104] (Example 1)

 Silver powder was produced using the silver powder production device
25 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
30 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
35 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.

A 0.50 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 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 616 seconds. The slurry generated before the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized was collected in a separate container and was not subjected to processes from solid-liquid separation onward.

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 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.

[0105] 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 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, 3.8 kg of silver powder was obtained.

[0106] 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.

The measurement results, etc. for the silver powder according to Example 1 are shown in Table 3. FIG. 3 is a graph of thermomechanical analysis of the silver powder according to Example 1. FIG. 4 is a graph illustrating an enlarged part (0 °C to 250 °C) of the graph in FIG. 3. FIG. 5 is an SEM photograph (20,000x magnification).

[0107] (Example 2)

A 0.153 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 0.008 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 3.15 L/min to adjust the pH. A 4.919 mol/L ammonia aqueous solution 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 0.106 mol/L.

A 0.478 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 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 1.55 m/sec (calculated from the combined flow rates of the silver nitrate aqueous solution, nitric acid aqueous solution, and ammonia aqueous solution). 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 1.04.

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 115 seconds. The slurry generated before the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized was collected in a separate container and was not subjected to processes from solid-liquid separation onward.

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 aqueous solution addition position was 0.48 seconds, the time from the ammonia aqueous solution addition position to the hydrazine aqueous solution addition position was 2.05 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 46.6 °C.

[0108] 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 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, 0.55 kg of silver powder was obtained.

[0109] The silver powder obtained in Example 2 was subjected to the same pulverization treatment as in Example 1.

The measurement results, etc. for the silver powder according to Example 2 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 2. FIG. 6 is an SEM photograph (20,000x magnification).

5 **[0110]** (Example 3)

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
10 double pipe, at a flow rate of 2.13 L/min to adjust the pH. A 4.436 mol/L ammonia aqueous solution 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
15 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,
20 complexing agent, reducing agent, and surface treatment agent was 0.115 mol/L.

A 0.50 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
25 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
30 (calculated from the combined flow rates of the silver nitrate aqueous solution, nitric acid aqueous solution, and ammonia aqueous solution). 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
35 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 617 seconds. The slurry generated before the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized was collected in a separate container and was not subjected to processes from solid-liquid separation onward.

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 aqueous solution addition position was 0.5 seconds, the time from the ammonia aqueous solution 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 47.4 °C.

[0111] 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 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, 3.6 kg of silver powder was obtained.

[0112] The silver powder obtained in Example 3 was subjected to the same pulverization treatment as in Example 1.

The measurement results, etc. for the silver powder according to Example 3 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 3. FIG. 7 is an SEM photograph (20,000x magnification).

[0113] (Example 4)

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 27.24 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 2.49 L/min to adjust the pH. A 4.436 mol/L

ammonia aqueous solution was introduced from the complexing agent supply pipe 6 (inner diameter: 6 mm), which is a coaxial double pipe, at a flow rate of 2.72 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 2.55 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.

A 0.50 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 2.97 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 1.74 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 1.75 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 568 seconds. The slurry generated before the flow of the silver ammine complex into which the surface treatment agent had been introduced stabilized was collected in a separate container and was not subjected to processes from solid-liquid separation onward.

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 0.43 seconds, the time from the nitric acid aqueous solution addition position to the ammonia aqueous solution addition position was 0.43 seconds, the time from the ammonia aqueous solution addition position to the hydrazine aqueous solution addition position was 1.82 seconds (2.1 m), and the time from the surface treatment agent addition position to the hydrazine aqueous solution

addition position was 0.10 seconds. The temperature of the silver ammine complex aqueous solution immediately before the hydrazine aqueous solution addition position was 47.3 °C.

[0114] The silver powder-containing slurry was discharged from the pipe 2.

5 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 impurities contained in the solid. The endpoint of washing was determined
10 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, 3.2 kg of silver powder was obtained.

[0115] The silver powder obtained in Example 4 was subjected to the same pulverization treatment as in Example 1.

15 The measurement results, etc. for the silver powder according to Example 4 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 4. FIG. 8 is an SEM photograph (20,000x magnification).

[0116] (Example 5)

20 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
25 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 having a stearic acid concentration of 0.08
30 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
35 adjuster, complexing agent, reducing agent, and surface treatment agent was 0.050 mol/L.

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 into which the surface treatment agent had been introduced stabilized was collected in a separate container and was not subjected to processes from solid-liquid separation onward.

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.

[0117] 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.

[0118] The silver powder obtained in Example 5 was subjected to the same pulverization treatment as in Example 1.

5 The measurement results, etc. for the silver powder according to Example 5 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 5. FIG. 9 is an SEM photograph (20,000x magnification).

[0119] (Example 6)

10 Silver powder according to Example 6 was obtained in the same manner as in Example 5, except that the concentration of ammonia water as a complexing agent was 3.144 mol/L and the operating time was 85 seconds. The obtained silver powder was 0.25 kg.

The silver powder obtained in Example 6 was subjected to the same pulverization treatment as in Example 1.

15 The measurement results, etc. for the silver powder according to Example 6 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 6. FIG. 10 is an SEM photograph (20,000x magnification).

[0120] (Example 7)

20 Silver powder according to Example 7 was obtained in the same manner as in Example 5, except that the concentration of ammonia water as a complexing agent was 3.041 mol/L and the operating time was 84 seconds. The obtained silver powder was 0.25 kg.

25 The silver powder obtained in Example 7 was subjected to the same pulverization treatment as in Example 1.

The measurement results, etc. for the silver powder according to Example 7 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 7. FIG. 11 is an SEM photograph (20,000x magnification).

30 **[0121]** (Example 8)

Silver powder according to Example 8 was obtained in the same manner as in Example 5, except that the concentration of ammonia water as a complexing agent was 2.728 mol/L and the operating time was 84 seconds. The obtained silver powder was 0.25 kg.

35 The silver powder obtained in Example 8 was subjected to the same pulverization treatment as in Example 1.

The measurement results, etc. for the silver powder according to Example 8 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Example 8. FIG. 12 is an SEM photograph (20,000x magnification).

5 **[0122]** (Comparative Example 1)

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.

10 2.28 g of a sodium hydroxide aqueous solution having a concentration 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
20 vacuum-dried at 73 °C.

[0123] 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 the silver powder was charged and disintegrated twice
25 for 90 seconds. As a result, the silver powder according to Comparative Example 1 was obtained.

[0124] The measurement results, etc. for the silver powder according to Comparative Example 1 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Comparative
30 Example 1. FIG. 13 is an SEM photograph (20,000x magnification).

[0125] (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
35 mass% (corresponding to 3 mol equivalents of ammonia per 1 mol of silver) 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
5 a first liquid. 142.7 g of an aqueous hydrazine hydrate solution having a 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
10 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.

[0126] The foregoing silver powder production was repeatedly performed
15 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 the silver powder was charged and disintegrated twice for 90 seconds. As a result, the silver powder according to Comparative Example 2 was obtained.

[0127] The measurement results, etc. for the silver powder according to Comparative Example 2 are shown in Table 3. FIGS. 3 and 4 are graphs of thermomechanical analysis of the silver powder according to Comparative Example 2. FIG. 14 is an SEM photograph (20,000x magnification).

[0128] Tables 1 and 2 show the production conditions in Examples 1 to 8 and
25 Comparative Examples 1 and 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	0.008	3.15	4.919	2.33	0.0155	2.19	Hydrazine	0.478	2.55
	3	Continuous	0.160	23.35	Nitric acid	0.024	2.13	4.436	2.33	0.0155	2.19	Hydrazine	0.500	2.55
	4	Continuous	0.160	27.24	Nitric acid	0.024	2.49	4.436	2.72	0.0155	2.55	Hydrazine	0.500	2.97
	5	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
	6	Continuous	0.070	23.35	Sodium carbonate	0.016	2.13	3.144	2.33	0.0804	2.19	Hydrazine carbonate	0.240	2.55
	7	Continuous	0.070	23.35	Sodium carbonate	0.016	2.13	3.041	2.33	0.0804	2.19	Hydrazine carbonate	0.240	2.55
	8	Continuous	0.070	23.35	Sodium carbonate	0.016	2.13	2.728	2.33	0.0804	2.19	Hydrazine carbonate	0.240	2.55
Comparative Example	1	Batch	-	-	-	-	-	-	-	-	-	-	-	-
	2	Batch	-	-	-	-	-	-	-	-	-	-	-	-

[0129] [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	0.106	1.55	1.49	1.04	115	0.55
	3	Continuous	0.115	1.50	1.49	1.01	617	3.6
	4	Continuous	0.115	1.75	1.74	1.01	568	3.2
	5	Continuous	0.050	1.50	1.49	1.01	83	0.24
	6	Continuous	0.050	1.50	1.49	1.01	85	0.25
	7	Continuous	0.050	1.50	1.49	1.01	84	0.25
	8	Continuous	0.050	1.50	1.49	1.01	84	0.25
Comparative Example	1	Batch	-	-	-	-	-	-
	2	Batch	-	-	-	-	-	-

[0130] [Table 2]

		BET specific surface area [m ² /g]	True density [g/cm ³]	D _{BET} [μm]	D _{SEM} [μm]	Particle size distribution			D ₅₀ /D _{BET}	Ig-loss [%]	Content of surface treatment agent [mass%]	Crystallite diameter	Thermal shrinkage ratio [%]	
						D ₁₀ [μm]	D ₅₀ [μm]	D ₉₀ [μm]				Dx [nm]	150°C	200°C
Example	1	1.16	9.99	0.52	0.45	0.22	0.57	0.99	1.10	0.62	0.480	38	0.89	1.32
	2	1.30	10.02	0.46	0.41	0.22	0.54	0.92	1.17	0.58	0.450	34	1.03	1.81
	3	1.12	10.01	0.54	0.51	0.24	0.63	1.13	1.18	0.58	0.470	35	0.68	1.02
	4	1.17	9.97	0.51	0.59	0.26	0.62	1.04	1.21	0.63	0.520	35	0.74	1.11
	5	1.72	9.84	0.34	0.23	0.13	0.31	0.65	0.91	0.93	0.710	30	1.07	2.23
	6	2.02	9.81	0.29	0.19	0.12	0.27	0.59	0.93	0.94	0.730	29	1.21	2.38
	7	1.81	9.80	0.32	0.21	0.12	0.27	0.57	0.86	1.01	0.810	27	1.36	2.48
	8	2.49	9.73	0.23	0.18	0.12	0.26	0.60	1.12	1.03	0.880	28	1.06	2.67
Comparative Example	1	1.04	10.07	0.57	0.51	0.313	0.83	1.50	1.45	0.52	0.440	45	0.50	0.88
	2	1.78	9.93	0.34	0.40	0.153	0.47	0.93	1.39	0.71	0.540	38	0.54	0.91

[0131] [Table 3]

[0132] (Paste Evaluation)

<Disconnection Rate and Volume Resistivity>

First, resin-curable conductive pastes were prepared using the silver powders obtained in Examples 1, 5, and 7 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 , 17 μm , 19 μm , and 21 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 disconnection rate and volume resistivity were 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. The disconnection rate was defined as the proportion of the number of line patterns exhibiting
 5 disconnection among the total of 20 line patterns, where 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
 10 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 (4):

$$\text{Volume resistivity } [\Omega \cdot \text{cm}] = \text{Line resistance } [\Omega] \times \text{Cross-sectional area } [\text{cm}^2] / \text{Line length } [\text{cm}] \quad (4).$$

The volume resistivity ($\Omega \cdot \text{cm}$) was calculated for line widths (design widths) of 15 μm and 19 μm . The line length (design length) used in measuring line resistance was 150 mm.

[0133] [Table 4]

	Volume resistivity [$\Omega \cdot \text{cm}$]		Disconnection rate [%]			
	15 μm	19 μm	15 μm	17 μm	19 μm	21 μm
Line width						
Example 1	7.7	7.8	0	10	0	0
Example 5	7.3	7.2	-	0	0	0
Example 7	7.1	7.4	0	0	0	0
Comparative Example 1	8.4	8.0	20	25	0	0
Comparative Example 2	8.1	8.7	0	0	10	0

[0134] As is clear from Table 4, with the silver powders according to Examples having 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, a ratio of D_{50} to D_{BET} of 1.3 or less, and a shrinkage ratio at 200 $^{\circ}\text{C}$ in thermomechanical analysis of
 25 1 % or more, the volume resistivity and the disconnection rate of fine lines formed by firing at a low temperature of 200 $^{\circ}\text{C}$ were low. This indicates that these silver powders are capable of imparting excellent volume resistivity and

fine-line printability to conductive pastes.

INDUSTRIAL APPLICABILITY

[0135] It is thus possible to provide a silver powder capable of, in the case of
5 being formed into a conductive paste, imparting excellent volume resistivity
and fine-line printability even when fired at low temperatures, a production
method for the silver powder, a silver powder production device capable of
producing the silver powder, and a resin-curable conductive paste having
excellent volume resistivity and fine-line printability even when fired at low
10 temperatures.

REFERENCE SIGNS LIST

	[0136]	1	silver powder production device
		2	pipe
15		4a	reducing agent supply pipe
		4b	reducing agent supply pipe
		5	surface treatment agent supply pipe
		6	complexing agent supply pipe
		7	pH adjuster supply pipe
20		10	reducing agent addition member
		11	opening
		12	slit portion
		13	gap

CLAIMS

- [Claim 1] A silver powder comprising:
a volume-based cumulative 50 % diameter D_{50} measured by a laser
5 diffraction method of 0.1 μm or more and 1.0 μm or less;
a ratio of D_{50} to BET diameter D_{BET} of 1.3 or less; and
a shrinkage ratio at 200 °C in thermomechanical analysis of 1 % or
more.
- 10 [Claim 2] The silver powder according to claim 1, comprising a shrinkage
ratio at 150 °C in thermomechanical analysis of 0.6 % or more.
- [Claim 3] The silver powder according to claim 1, comprising a BET
specific surface area of 0.90 m^2/g or more and 2.50 m^2/g or less.
15
- [Claim 4] The silver powder according to any one of claims 1 to 3, for
use in a resin-curable conductive paste.
- [Claim 5] A silver powder production method comprising:
20 flowing a 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;
25 adding a hydrazine-based reducing agent to the flow path at a reducing
agent addition position downstream of the complexing agent addition position;
and
reducing and precipitating silver powder in the flow path.
- 30 [Claim 6] The silver powder production method according to claim 5,
wherein a time required for the silver-containing solution to flow from the
complexing agent addition position to the reducing agent addition position is
0.1 seconds or more and 10 seconds or less.
- 35 [Claim 7] The silver powder production method according to claim 5,
comprising adding a surface treatment agent to the flow path between the

complexing agent addition position and the reducing agent addition position, or downstream of the reducing agent addition position.

[Claim 8] A silver powder production device that adds a pH adjuster, a
5 complexing agent, and a hydrazine-based reducing agent as a reducing agent
to a silver-containing solution to reduce and precipitate silver powder, the
silver powder production device comprising:
 a pipe forming a flow path of the silver-containing solution;
 a pH adjuster addition portion connected to the pipe;
10 a complexing agent addition portion; and
 a reducing agent addition portion connected to the pipe downstream of
the nitric acid addition portion and the complexing agent addition portion.

[Claim 9] A resin-curable conductive paste comprising the silver powder
15 according to any one of claims 1 to 3.