

## Description

Title of Invention: SILVER PARTICLE SPHERICAL AGGREGATE  
AND SPHERICAL SILVER PARTICLES OBTAINED BY CRUSHING SAME

### Technical Field

[0001] The present invention relates to a silver particle spherical aggregate. Specifically, the present invention relates to a nano silver particle spherical aggregate in which spherical nano silver particles are spherically aggregated, and a silver particle spherical aggregate obtained by subjecting the nano silver particle spherical aggregate to heat treatment. Both silver particle spherical aggregates can be suitably used as a conductive filler, can be subjected to disintegration treatment to produce spherical silver particles, are silver particle spherical aggregates having excellent dispersibility, and are silver particle spherical aggregates having excellent handleability.

### Background Art

[0002] With respect to silver particles, applications as a conductive paste filler (hereinafter referred to as "conductive filler") used to form electrodes, circuits, and the like, are expanding.

[0003] Further, as a result of progress in fine patterning of electrodes and circuits in the

aforementioned applications, monodisperse spherical silver microparticles having characteristics of microparticle size, sharp particle size distribution, and high dispersibility are required in recent years.

[0004] However, in the production of monodisperse spherical silver microparticles having microparticle size, sharp particle size distribution, and high dispersibility, there are problems in that, for example, a special process employing two-step reduction or seed particles is required, and an apparatus for allowing collision in the air is required.

[0005] In addition, there are problems in that the monodisperse spherical silver microparticles produced are difficult to be separated and recovered, and have poor handleability.

[0006] Thus, development of monodisperse spherical silver microparticles that can be produced by a simple method and have excellent handleability is desired.

#### Citation List

##### Patent Literature

[0007]

Patent Literature 1: Japanese Patent Laid-Open No. 2005-048237

Patent Literature 2: Japanese Patent Laid-Open No. 2015-129352

Patent Literature 3: Japanese Patent Laid-Open No. 2006-225760

Summary of Invention

Technical Problem

[0008] Patent Literature 1 describes a method for producing silver particles, including contacting and mixing an organic reducing agent with an aqueous silver ammine complex solution, and maintaining the silver concentration and the organic reducing agent concentration in the mixed solution in a certain range to reduce and precipitate silver particles, whereby silver particles being fine particles and having excellent dispersibility can be obtained.

[0009] However, the production method described in Patent Literature 1 requires reduction using two flow paths, and the silver particles produced are fine and difficult to be separated and recovered, and have poor handleability, which are problematic.

[0010] Patent Literature 2 describes a method for producing silver particles, including contacting and mixing an aqueous silver ammine complex solution with an aqueous reducing agent solution in the air to reduce and precipitate silver particles, thereby avoiding a phenomenon of the resulting silver particles adhering to the flow path wall, whereby silver particles having small particle size, sharp particle size distribution, and

excellent dispersibility can be obtained without generating aggregated silver particles.

[0011] However, the method described in Patent Literature 2 requires a special apparatus for contacting and mixing them in the air, and the silver particles produced are fine and difficult to be separated and recovered, and have poor handleability, which are problematic.

[0012] Patent Literature 3 describes a method for producing silver particles by reacting a silver compound solution and a reducing agent solution in the presence of at least one selected from the group consisting of aliphatic unsaturated dicarboxylic acid, an anhydride thereof, and a salt thereof.

[0013] While the method described in Patent Literature 3 can produce spherical silver particles, the average particle size is as large as 0.5  $\mu\text{m}$  to 5  $\mu\text{m}$ , and fine silver particles cannot be produced, which are problematic.

[0014] As a result of intensive studies to solve the above problems, the present inventors have found a remarkable knowledge that a nano silver particle spherical aggregate in which spherical nano silver particles having a BET diameter of 20 nm or more and 100 nm or less are aggregated, the nano silver particle spherical aggregate having a value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 10 or more has excellent

dispersibility and handleability, can be suitably used as a conductive filler, can be subjected to disintegration treatment to produce spherical nano silver particles, can be subjected to heat treatment to produce a silver particle spherical aggregate in which spherical submicron silver particles are aggregated, and further, can be produced by a simple method, thereby solving the above technical problems.

#### Solution to Problem

[0015] The technical problems described above can be solved by the present invention as follows.

[0016] The present invention is a nano silver particle spherical aggregate in which spherical nano silver particles having a BET diameter of 20 nm or more and 100 nm or less are aggregated, the nano silver particle spherical aggregate having a value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 10 or more.

[0017] The present invention is further the nano silver particle spherical aggregate in which the D50% particle size measured by a laser diffraction particle size measurement method is 1.0  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less, and a BET specific surface area is 6.0  $\text{m}^2/\text{g}$  or more and 30.0  $\text{m}^2/\text{g}$  or less.

[0018] The present invention is a silver particle spherical aggregate obtained by subjecting the nano silver particle spherical aggregate to heat treatment.

[0019] The present invention is the silver particle spherical aggregate, that is a silver particle aggregate in which spherical submicron silver particles having a BET diameter of 120 nm or more and 400 nm or less are aggregated, wherein the silver particle aggregate has a value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 2 or more and 100 or less.

[0020] The present invention is the silver particle spherical aggregate, in which the D50% particle size measured by a laser diffraction particle size measurement method is 1.0  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less, and a BET specific surface area is 1.5  $\text{m}^2/\text{g}$  or more and 5.0  $\text{m}^2/\text{g}$  or less.

[0021] The present invention is the silver particle spherical aggregate, in which a hydrogen loss is 1.0% by mass or less.

[0022] The present invention is spherical silver particles obtained by subjecting the silver particle spherical aggregate to disintegration treatment.

[0023] The present invention is a method for producing the nano silver particle spherical aggregate, including adding at least one of phthalic acid, phthalic anhydride, or a phthalic acid salt to a silver compound solution and

a reducing agent solution to produce the nano silver particle spherical aggregate.

#### Advantageous Effects of Invention

[0024] The present invention is an aggregate composed of spherical nano silver particles having a BET diameter of 20 nm or more and 100 nm or less, and the aggregate has a value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 10 or more, is a spherical aggregate, and is thus an aggregate in which nano silver particles having excellent handleability and excellent dispersibility are spherically aggregated.

[0025] The nanoparticle spherical aggregate of the present invention can be handled as spherical silver particle powder, and can be suitably used as a conductive filler.

[0026] When the D50% particle size measured by a laser diffraction particle size measurement method of the nano silver particle spherical aggregate of the present invention is 1.0  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less and the BET specific surface area is 6.0  $\text{m}^2/\text{g}$  or more and 30.0  $\text{m}^2/\text{g}$  or less, a nano silver particle spherical aggregate having handleability as silver particle powder on the order of micrometers can be obtained.

[0027] When the nano silver particle spherical aggregate is subjected to disintegration treatment, spherical nano

silver particles are obtained, which have performance as fine silver particle powder on the order of nanometers, and thus can be suitably used as a conductive filler.

[0028] When the nano silver particle spherical aggregate is subjected to heat treatment, spherical nano silver particles that constitute the nano silver particle spherical aggregate grow into spherical submicron silver particles, and thus the silver particle spherical aggregate in which spherical submicron silver particles are aggregated can be produced.

[0029] In addition, an additive and the like are decomposed by heat treatment, so that a silver particle spherical aggregate having high purity can be obtained.

[0030] In addition, constituent particles can be made into spherical submicron silver particles of a desired size by heat treatment.

[0031] In particular, the aggregate composed of spherical submicron silver particles having a BET diameter of 120 nm or more and 400 nm or less is spherical and the hydrogen loss can be 1.0% by mass or less, so that a silver particle spherical aggregate having excellent conductivity is obtained and can be suitably used as a conductive filler.

[0032] When the silver particle spherical aggregate is subjected to disintegration treatment, spherical submicron silver particles are obtained and can be suitably used as a conductive filler.

## Brief Description of Drawings

[0033]

[Figure 1] Figure 1 is an SEM photograph (5000 times) of a nano silver particle spherical aggregate of the present invention (Example 1).

[Figure 2] Figure 2 is an SEM photograph (5000 times) of a silver particle spherical aggregate of the present invention (Reference Example 3).

[Figure 3] Figure 3 is an SEM photograph (20000 times) of a nano silver particle spherical aggregate of the present invention subjected to heat treatment and then subjected to disintegration treatment (Reference Example 10).

[Figure 4] Figure 4 is an SEM photograph (5000 times) of Comparative Example 8.

[Figure 5] Figure 5 is an SEM photograph (10000 times) of Comparative Example 8 after being subjected to heat treatment.

## Description of Embodiments

[0034] The present invention is a nano silver particle spherical aggregate in which spherical nanoparticles having a BET diameter of 20 nm or more and 100 nm or less are spherically aggregated.

[0035] When the BET diameter is less than 20 nm or more than 100 nm, a spherical aggregate may not be formed, and particles may not grow even after heat treatment.

[0036] In the nano silver particle spherical aggregate of the present invention, the value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] is preferably 10 or more, more preferably 10 or more and 300 or less, and still more preferably 20 or more and 200 or less.

[0037] The value of [D50% particle size]/[BET diameter] is a value indicating the degree of aggregation of the aggregate. If the value is less than 10, handleability may be deteriorated due to low degree of aggregation, or constituent silver particles may not grow into spherical submicron silver particles even after heat treatment.

[0038] In the nano silver particle spherical aggregate of the present invention, the D50% particle size measured by a laser diffraction particle size measurement method is preferably 1.0  $\mu\text{m}$  to 10.0  $\mu\text{m}$  or less, more preferably 1.0  $\mu\text{m}$  to 6.0  $\mu\text{m}$ , and still more preferably 2.0  $\mu\text{m}$  to 4.0  $\mu\text{m}$ .

[0039] If the particle size is less than 1.0  $\mu\text{m}$ , handleability is deteriorated. If it is more than 10.0  $\mu\text{m}$ , coarse particles may be generated, which are not suitable as a fine conductive filler.

[0040] In the nano silver particle spherical aggregate of the present invention, the BET specific surface area is preferably 6.0  $\text{m}^2/\text{g}$  to 30.0  $\text{m}^2/\text{g}$ , and more preferably 6.0  $\text{m}^2/\text{g}$  to 20.0  $\text{m}^2/\text{g}$ .

[0041] If the BET specific surface area is less than 6.0  $\text{m}^2/\text{g}$ , constituent silver particles may not grow into

spherical submicron silver particles even after heat treatment or may not become spherical nano silver particles by disintegration treatment, so that the production of an aggregate of 30 m<sup>2</sup>/g or more is difficult.

[0042] The nano silver particle spherical aggregate of the present invention can be produced by adding at least one of phthalic acid, phthalic anhydride, or a phthalic acid salt to a silver compound solution and a reducing agent solution.

[0043] (Silver compound solution)

The silver compound in the present invention is not particularly limited, as long as it can react with a reducing agent to produce silver particles.

[0044] Examples of the silver compound include silver nitrate, silver carbonate, and silver acetate, and silver nitrate is preferably used in terms of costs.

[0045] As the solvent for dissolving the silver compound, water and/or an alcohol is preferably used.

[0046] (Reducing agent solution)

The reducing agent in the present invention is not limited, as long as the reducing agent mixed with the silver compound solution reduces the silver compound to precipitate silver particles.

[0047] Examples of the reducing agent include L-ascorbic acid, D-erythorbic acid, salts of L-ascorbic acid or D-

erythorbic acid, hydrazine, a hydrazine compound, formaldehyde, formic acid, and glucose.

[0048] As the solvent for dissolving the reducing agent, water and/or an alcohol is preferably used.

[0049] In the present invention, one or more of phthalic acid, phthalic anhydride, and a phthalic acid salt (hereinafter referred to as "phthalic acid and the like") are used as an additive.

[0050] It is presumed that phthalic acid and the like have an effect of reducing the primary particle size of spherical nano silver particles and also have an effect of adjusting the aggregation state of spherical nano silver particles to a particle shape close to a true sphere.

[0051] By forming the aggregation state of a true sphere shape, the contact area is reduced, so that further aggregation can be prevented and dispersibility can be increased.

[0052] The amount of phthalic acid and the like added differs depending on the type of phthalic acid and the like to be used, and is preferably 3.0 parts by weight or more and 25.0 parts by weight or less relative to 100 parts by weight of the amount of silver contained in the silver compound solution (amount in terms of metal).

[0053] If the amount of phthalic acid added is less than 3.0 parts by weight, the primary particle size is not

sufficiently small, and a true spherical aggregate may not be obtained.

[0054] If the amount of phthalic acid added is more than 25.0 parts by weight, it is difficult to dissolve phthalic acid in the silver nitrate solution, and thus a nano silver particle spherical aggregate containing impurities may be generated.

In addition, the entire concentration needs to be significantly reduced for dissolution, and costs are increased.

[0055] It is preferable that phthalic acid and the like be mixed in at least either the silver compound solution or the reducing agent solution, and then the silver compound solution and the reducing agent solution be mixed for production.

[0056] The mixing method is not particularly limited, and may be any of a method of simultaneously adding the silver compound solution and the reducing agent solution to a reaction vessel, a method of adding the reducing agent solution to the silver compound solution, and a method of adding the silver compound solution to the reducing agent solution.

[0057] The temperature of the silver compound solution and the reducing agent solution in a mixture is preferably 50°C or less, more preferably 15°C to 35°C, and still more preferably 20°C to 30°C.

[0058] If the temperature is more than 50°C, the primary particle size of spherical silver particles may be too large. If the temperature is less than 15°C, it is difficult to dissolve the additive, and silver particle powder containing impurities may be generated.

In addition, the entire concentration needs to be significantly reduced for dissolution, and costs are increased.

[0059] The pH of the mixed solution may be any value within a range of the chemical to be used.

[0060] The precipitated silver particles can be easily separated from the reaction solution by filtration and the like. After separation, the silver particles can be washed with water or an alcohol, and then dried to produce the nano silver particle spherical aggregate.

[0061] In the nano silver particle spherical aggregate of the present invention, the spherical nano silver particles that constitute the spherical aggregate can be grown by heat treatment, so that a silver particle spherical aggregate composed of the grown spherical submicron silver particles can be produced.

[0062] The heat treatment temperature is preferably 200°C to 250°C, and more preferably 230°C to 250°C.

[0063] If the temperature of the heat treatment is less than 200°C, the organic substance on the surface is not decomposed and particle growth does not proceed. If the

temperature is more than 250°C, it is difficult to obtain a desired particle size due to rapid particle growth.

[0064] The heat treatment time depends on the temperature, and is preferably 1 hour to 3 hours.

[0065] If the heat treatment time is less than 1 hour, the organic substance on the surface is not sufficiently decomposed and particle growth does not proceed. If it is more than 3 hours, aggregation proceeds and dispersibility may be lost.

[0066] The apparatus to be used in the heat treatment is not particularly limited, and may be an apparatus that allows heating to about 300°C and can uniformly maintain the inside of the heating chamber at a predetermined temperature for a certain time.

[0067] If the inside of the heating chamber cannot be uniformly heated and maintained, the particle growth of the nano silver particles that constitute a nano silver particle aggregate is non-uniform, resulting in a large variation of the particle size of the spherical submicron silver particles constituting the silver particle aggregate obtained by heat treatment.

[0068] The atmosphere in the heat treatment is not particularly limited, and heat treatment may be performed in any atmosphere such as air, nitrogen, and hydrogen.

[0069] The silver particle spherical aggregate of the present invention is a silver particle spherical

aggregate of high purity because impurities are decomposed by the heat treatment.

[0070] The BET diameter of the spherical silver particles grown by the heat treatment is preferably 120 nm or more and 400 nm or less.

[0071] When the BET diameter is less than 120 nm or more than 400 nm, the aggregate may not be spherical.

[0072] The value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of the spherical aggregate of silver particles of the present invention is preferably 2 or more and 100 or less, and more preferably 5 or more and 30 or less.

[0073] If [D50% particle size]/[BET diameter] is less than 2, the degree of aggregation is low and handleability is deteriorated. If it is more than 100, spherical submicron silver particles may not be formed even after disintegration treatment.

[0074] In the silver particle spherical aggregate of the present invention, the D50% particle size measured by the laser diffraction particle size measurement method is preferably 1.0  $\mu\text{m}$  to 10.0  $\mu\text{m}$  or less, more preferably 1.0  $\mu\text{m}$  to 6.0  $\mu\text{m}$ , and still more preferably 2.0  $\mu\text{m}$  to 4.0  $\mu\text{m}$ .

[0075] If the particle size is less than 1.0  $\mu\text{m}$ , handleability is deteriorated. If it is more than 10.0  $\mu\text{m}$ , coarse particles may be generated and are not suitable as a fine conductive filler.

[0076] In the silver particle spherical aggregate of the present invention, the BET specific surface area is 1.5 m<sup>2</sup>/g to 5.0 m<sup>2</sup>/g, and more preferably 2.0 m<sup>2</sup>/g to 4.0 m<sup>2</sup>/g.

[0077] If the BET specific surface area is less than 1.5 m<sup>2</sup>/g, the heat treatment proceeds too much and excess aggregation may occur. If it is more than 5.0 m<sup>2</sup>/g, the heat treatment does not proceed and the particles may not be grown into spherical submicron silver particles.

[0078] In the silver particle spherical aggregate of the present invention, the hydrogen loss is preferably 1.0% by mass or less, more preferably 0.8% by mass or less, and still more preferably 0.5% by mass or less.

[0079] When the hydrogen loss is 1.0% by mass or less, the silver particle spherical aggregate has excellent conductivity and thus can be suitably used as a conductive filler.

[0080] By subjecting the nano silver particle spherical aggregate and the silver particle spherical aggregate of the present invention to disintegration treatment, the spherical nano silver particles and the spherical submicron silver particles can be produced.

[0081] The disintegration treatment method may be either dry or wet, and is not particularly limited. A known disintegration treatment method and apparatus may be used.

[0082] Examples of the disintegration treatment method include disintegration treatment using roll kneading or a jet mill.

#### Examples

[0083] The present invention will be described with reference to Examples and Comparative Examples, but the present invention is not limited thereto.

The evaluation methods of Examples and Comparative Examples are shown in Table 5.

[0084] (Example 1)

50.0 g of silver nitrate and 4.0 g of phthalic acid were dissolved in 1000 mL of pure water to prepare a silver compound solution with a solution temperature of 26°C.

[0085] 26.8 g of ascorbic acid was dissolved in 1000 mL of pure water to prepare a reducing agent solution with a solution temperature of 26°C.

[0086] The reducing agent solution was added to the silver compound solution prepared, and the mixture was stirred for 10 minutes to react them.

The resulting precipitate was filtered, washed, and then dried at 40°C for 3 hours.

[0087] The nano silver particle aggregate of Example 1 is shown in Figure 1.

As shown in Figure 1, the nano silver particle aggregate of Example 1 is found to have a substantially true spherical shape and to be monodisperse.

[0088] Each Comparative Example was produced in the same manner as in Example 1, except that the additive was changed as described in Table 1.

[0089]

[Table 1]

|                       | Additive         | Amount added (parts by weight) | Amount of silver (parts by weight) | BET (m <sup>2</sup> /g) | BET diameter (nm) | D50% (μm) | D50% /BET diameter | HL (%) | Shape (constituent particles) |
|-----------------------|------------------|--------------------------------|------------------------------------|-------------------------|-------------------|-----------|--------------------|--------|-------------------------------|
| Example 1             | Phthalic acid    | 12.7                           | 100                                | 16.16                   | 35                | 4.095     | 115.8              | 2.04   | Spherical (spherical powder)  |
| Comparative Example 1 | Maleic acid      | 12.7                           | 100                                | 1.95                    | 293               | 5.579     | 19.0               | 0.41   | Spherical (flat powder)       |
| Comparative Example 2 | Oxalic acid      | 12.7                           | 100                                | 0.33                    | 1732              | 19.691    | 11.4               | 0.41   | Irregular shape               |
| Comparative Example 3 | Succinic acid    | 12.7                           | 100                                | 0.8                     | 714               | 7.452     | 10.4               | 0.13   | Irregular shape               |
| Comparative Example 4 | Isophthalic acid | 12.7                           | 100                                | 2.21                    | 259               | 1.868     | 7.2                | 10.18  | Irregular shape               |
| Comparative Example 5 | Benzoic acid     | 12.7                           | 100                                | 0.58                    | 985               | 3.996     | 4.1                | 0.38   | Spherical (flat powder)       |

[0090] When an additive other than phthalic acid is used, the shape of the aggregate was not spherical, or constituent silver particles (constituent particles) were not spherical, while the shape of the aggregate was spherical.

[0091] Then, nano silver particle aggregates were produced in the same manner as in Example 1, except that the amount of phthalic acid added was changed as described in Table 2.

[0092]

[Table 2]

|                     |   | Additive      | Amount added (parts by weight) | Amount of silver (parts by weight) | BET (m <sup>2</sup> /g) | BET diameter (nm) | D50% (μm) | D50% /BET diameter | HL (%) | Shape (constituent particles) |
|---------------------|---|---------------|--------------------------------|------------------------------------|-------------------------|-------------------|-----------|--------------------|--------|-------------------------------|
| Example             | 1 | Phthalic acid | 12.7                           | 100                                | 16.16                   | 35                | 4.095     | 115.8              | 2.04   | Spherical (spherical powder)  |
|                     | 2 | Phthalic acid | 4.0                            | 100                                | 6.79                    | 84                | 3.491     | 41.5               | 1.41   | Spherical (spherical powder)  |
|                     | 3 | Phthalic acid | 5.0                            | 100                                | 8.99                    | 64                | 3.294     | 51.8               | 1.59   | Spherical (spherical powder)  |
|                     | 4 | Phthalic acid | 6.3                            | 100                                | 11.95                   | 48                | 3.045     | 63.7               | 1.9    | Spherical (spherical powder)  |
|                     | 5 | Phthalic acid | 25.0                           | 100                                | 14.8                    | 39                | 2.418     | 62.6               | 2.11   | Spherical (spherical powder)  |
| Comparative Example | 6 | Phthalic acid | 0.5                            | 100                                | 0.79                    | 723               | 3.552     | 4.9                | 0.89   | Dendritic shape               |
|                     | 7 | Phthalic acid | 1.0                            | 100                                | 1.26                    | 454               | 3.525     | 7.8                | 0.84   | Dendritic shape               |
|                     | 8 | Phthalic acid | 3.0                            | 100                                | 3.62                    | 158               | 3.01      | 19.1               | 1.23   | Spherical (flat powder)       |

[0093] When the amount of phthalic acid added was small, the shape of the aggregate was not spherical, or constituent silver particles (constituent particles) were not spherical, while the aggregate was spherical. The silver particle aggregate of Comparative Example 8 is shown in Figure 4.

[0094] Since the amount of phthalic acid added was small in Comparative Example 8, the BET diameter of the silver particles that constitute the silver particle aggregate was large, and a part of the constituent silver particles was aggregated into coarse powder (an arrow portion in Figure 5) even after heat treatment at 230°C for 1.5

hours, so that spherical submicron silver particles were not formed (Figure 5).

[0095] The nano silver particle aggregate obtained in Example 1 was put in a container, subjected to heat treatment at a temperature described in Table 3, taken out from an oven, and cooled to give a silver particle spherical aggregate.

All of these operations were performed in the air atmosphere.

[0096]

[Table 3]

| Reference Example | Additive      | Amount added (parts by weight) | Amount of silver (parts by weight) | Temperature (°C) | Time (h) | BET (m <sup>2</sup> /g) | BET diameter (nm) | D50% (μm) | D50% /BET diameter | HL (%) |
|-------------------|---------------|--------------------------------|------------------------------------|------------------|----------|-------------------------|-------------------|-----------|--------------------|--------|
| 1                 | Phthalic acid | 12.7                           | 100                                | 200              | 1        | 3.57                    | 160               | 3.478     | 21.7               | 0.87   |
| 2                 | Phthalic acid | 12.7                           | 100                                | 230              | 1        | 2.86                    | 200               | 3.178     | 15.9               | 0.72   |
| 3                 | Phthalic acid | 12.7                           | 100                                | 230              | 2        | 2.81                    | 203               | 3.397     | 16.7               | 0.49   |
| 4                 | Phthalic acid | 12.7                           | 100                                | 230              | 3        | 2.49                    | 229               | 3.491     | 15.2               | 0.4    |
| 5                 | Phthalic acid | 12.7                           | 100                                | 250              | 1        | 2.64                    | 216               | 3.56      | 16.4               | 0.22   |
| 6                 | Phthalic acid | 12.7                           | 100                                | 100              | 1        | 7.2                     | 79                | 4.183     | 52.7               | 1.18   |
| 7                 | Phthalic acid | 12.7                           | 100                                | 150              | 1        | 5.99                    | 95                | 4.144     | 43.4               | 1.14   |
| 8                 | Phthalic acid | 12.7                           | 100                                | 270              | 1        | 0.66                    | 866               | 3.025     | 3.5                | 0.08   |
| 9                 | Phthalic acid | 12.7                           | 100                                | 230              | 6        | 1.63                    | 351               | 3.498     | 10.0               | 0.32   |

[0097] It is found from Table 3 that desired silver particle spherical aggregates in which spherical submicron silver particles are aggregated can be produced depending on the heating temperature and the heating

time. The silver particle spherical aggregate of Reference Example 3 is shown in Figure 2.

[0098] The silver particle spherical aggregate obtained by heat treatment was subjected to disintegration treatment by performing roll kneading using three rolls (manufactured by AIMEX CO., Ltd.) with 5 passes, a clearance of 0.03 mm, rotational speed: 30 Hz (feed roll: 23, center roll: 63.5, and apron roll: 175 (rpm)), and silver:solvent = 8:2 (weight ratio).

[0099] The electrical resistivities ( $10^{-6} \Omega \cdot \text{cm}$ ) of the submicron silver particles after disintegration treatment are shown in Table 4.

[Table 4]

| Reference Example | BET ( $\text{m}^2/\text{g}$ ) | BET diameter (nm) | HL (%) | Electrical resistivity ( $\times 10^{-6} \Omega \cdot \text{cm}$ ) |
|-------------------|-------------------------------|-------------------|--------|--------------------------------------------------------------------|
| 10                | 2.81                          | 203               | 0.49   | 3.76                                                               |
| 11                | 0.81                          | 705               | 1.00   | 4.58                                                               |
| 12                | 4.76                          | 120               | 1.35   | 40.7                                                               |
| 13                | 2.52                          | 227               | 1.24   | 38.5                                                               |
| 14                | 2.11                          | 271               | 0.55   | 41.0                                                               |
| 15                | 1.82                          | 314               | 0.51   | 33.3                                                               |

[0100] It was demonstrated from Table 4 that the submicron silver particles (Reference Example 10/Figure 3), which were obtained by subjecting the silver particle spherical aggregate obtained by heat treatment to disintegration treatment and had a BET diameter in a range of 120 nm to 400 nm, have low electrical resistivity and can be suitably used as a conductive filler.

[Table 5]

| Properties             | Evaluation method                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
|------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| D50%                   | Laser diffraction particle size distribution measurement apparatus SALD-2300 (manufactured by SHIMADZU CORPORATION)<br>Cumulative 50% particle size on a volume basis                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |
| BET                    | BET specific surface area measurement apparatus Macsorb (manufactured by MOUNTECH Co., Ltd.)<br>* BET flow method (one point method) based on JIS Z 8830                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| BET diameter           | BET diameter = $6/(\text{density of Ag} \times \text{BET})$<br>Density of Ag: $10.5 \text{ g/cm}^3$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
| D50%/BET diameter      | Ratio of D50% ( $\mu\text{m}$ ) to BET diameter ( $\mu\text{m}$ )                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |
| Hydrogen loss (HL)     | Amount of sample: 2 g, Temperature: $800^\circ\text{C}$ , Heating time: 0.5 h<br>Atmosphere: $\text{H}_2$ , $\text{H}_2$ gas flow rate: $0.5 \text{ L/min}$<br>$\text{HL}(\%) = [(\text{Sample weight before heating (g)} - \text{Sample weight after heating (g)}) / \text{Sample weight before heating (g)}] \times 100$                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |
| Electrical resistivity | $R \times w \times t/L$<br>R: resistance value ( $\Omega$ ), w: width (cm), t: thickness (cm), L: length (cm)<br>The solvent was added to each silver powder at 80:20 in wt% to prepare a dispersion paste.<br>This was applied in a certain film thickness, and the temperature was increased to $300^\circ\text{C}$ at a temperature increasing rate of $5^\circ\text{C/min}$ and held for 10 minutes to prepare a silver coating film, and the electrical resistivity thereof was measured.<br>The resistance value (R) was measured by the four-point probe method by setting $L = 4 \text{ cm}$ and using milliohm HiTESTER 3540 (manufactured by HIOKI E.E. CORPORATION).<br>The width (w) and the thickness (t) of the coating film were measured using a surface roughness meter (surface roughness measurement device SE-1700 $\alpha$ /manufactured by Kosaka Laboratory Ltd.). |

#### Industrial Applicability

[0101] The present invention relates to a nano silver particle spherical aggregate in which spherical nano silver particles are spherically aggregated, and a silver particle spherical aggregate obtained by subjecting the nano silver particle spherical aggregate to heat treatment. Both silver particle spherical aggregates can

be suitably used as a conductive filler, can be subjected to disintegration treatment to produce spherical silver particles, are monodisperse, and have excellent handleability.

Therefore, the present invention has a high industrial applicability.

## Claims

### [Claim 1]

A nano silver particle spherical aggregate in which spherical nano silver particles having a BET diameter of 20 nm or more and 100 nm or less are aggregated, the nano silver particle spherical aggregate having a value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 10 or more.

### [Claim 2]

The nano silver particle spherical aggregate according to claim 1, wherein the D50% particle size measured by a laser diffraction particle size measurement method is 1.0  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less, and a BET specific surface area is 6.0  $\text{m}^2/\text{g}$  or more and 30.0  $\text{m}^2/\text{g}$  or less.

### [Claim 3]

A silver particle spherical aggregate obtained by subjecting the nano silver particle spherical aggregate according to claim 1 or 2 to heat treatment.

### [Claim 4]

The silver particle spherical aggregate according to claim 3, that is a silver particle aggregate in which spherical submicron silver particles having a BET diameter of 120 nm or more and 400 nm or less are aggregated, wherein the silver particle aggregate has a

value of [D50% particle size measured by laser diffraction particle size measurement method]/[BET diameter] of 2 or more and 100 or less.

[Claim 5]

The silver particle spherical aggregate according to claim 3, wherein the D50% particle size measured by a laser diffraction particle size measurement method is 1.0  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less, and a BET specific surface area is 1.5  $\text{m}^2/\text{g}$  or more and 5.0  $\text{m}^2/\text{g}$  or less.

[Claim 6]

The silver particle spherical aggregate according to claim 3, wherein a hydrogen loss is 1.0% by mass or less.

[Claim 7]

Spherical silver particles obtained by subjecting the silver particle spherical aggregate according to claim 1 or claim 3 to disintegration treatment.

[Claim 8]

A method for producing the nano silver particle spherical aggregate according to claim 1 or 2, comprising adding at least one of phthalic acid, phthalic anhydride, or a phthalic acid salt to a silver compound solution and a reducing agent solution to produce the nano silver particle spherical aggregate.