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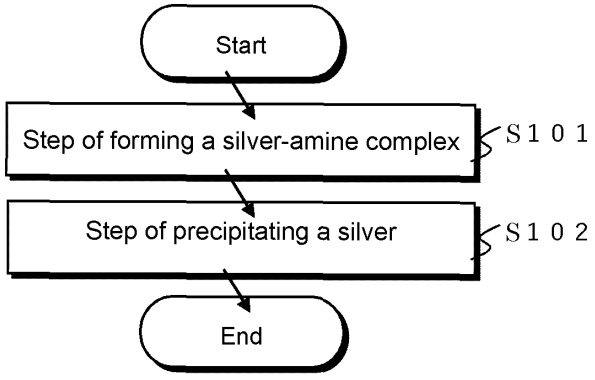
(54) METHOD FOR PRODUCING SILVER NANOPARTICLES

(57) Provided is a method for producing silver nanoparticles having high monodispersity. The method for producing silver nanoparticles comprises steps of: forming a silver-amine complex as a precursor by reacting a silver compound with an amine compound in the presence of a dispersant; and precipitating a silver nanoparticle from a chemical reaction system containing the silver-amine complex, wherein the amine compound contains at least one compound represented by chemical formula (1).

【Fig.1】



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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing silver nanoparticles.

BACKGROUND

[0002] Silver nanoparticles absorb and scatter light much more than ordinary dyes and pigments. Silver nanoparticles may be used for analysis such as surface-enhanced Raman spectroscopy, and applied to diagnostic agents, paints, and the like because of their optical characteristics. The optical characteristics of these silver nanoparticles are due to a phenomenon called plasmon resonance, which occurs when the electric field oscillation of light resonates with the free electrons in the metal. The intensity of light absorption in the plasmon resonance allows silver nanoparticles to be applied for various uses as described above.

[0003] In addition, the absorption wavelength of light in this plasmon resonance varies with the particle diameter (becomes longer in proportion to the particle diameter). Adjusting the particle diameter appropriately is capable of achieving desired optical characteristics. Thus, when silver nanoparticles are used as a coloring agent for a metallic glossy ink or the like, a metallic glossy film with an adjusted color is possible to be produced.

[0004] However, obtaining silver nanoparticles having desirable optical characteristics as described above requires a synthesis of particles having high monodispersity. A commonly used method for synthesizing silver nanoparticles is a chemical reduction method in which a silver salt such as silver nitrate as a starting material is reacted with a reducing agent in a solvent such as water to obtain silver nanoparticles.

[0005] For example, in Patent Literature 1, silver particles are synthesized using an alkanolamine as a reducing agent in the presence of a polymer-based dispersant. However, the synthesis method described in Patent Literature 1 has the following problem. The synthesis method described in Patent Literature 1 uses dimethylaminoethanol or methyldiethanolamine as the alkanolamine. However, these tertiary amines have low coordinative ability to silver ions due to steric hindrance, and have difficulty in forming silver-amine complexes. For this reason, silver ions precipitate as silver oxide due to a change in pH caused by the addition of amine, and the reaction system becomes heterogeneous. As a result, the produced silver particles have a wide particle diameter distribution.

[0006] In addition, since these tertiary amines have a higher reducing power than those of primary and secondary amines, the reaction rate is excessively high, the particle diameter of the produced particles becomes inconsistent and aggregation of the produced particles is occurred.

[0007] Meanwhile, Patent Literature 2 proposes a method for obtaining silver particles by forming a silver-alkanolamine complex, which is then further reacted with a reducing agent such as L-ascorbic acid. In this synthesis method, complex formation is performed to synthesize silver nanoparticles in a uniform reaction system. However, the synthesis method described in Patent Literature 2 has the following problem. In the synthesis method described in Patent Literature 2, L-ascorbic acid or the like is added as a reducing agent, but the reducing agent has a coordinative ability to silver, so that a compound other than the previously added amine coordinates to the silver particle surface. In this case, two types of compounds (L-ascorbic acid and alkanolamine) compete as reducing agents or surface protecting agents, so that particles having multiple particle size distributions are produced.

[0008] In addition, there is a case where diethanolamine, which is a secondary amine, is used as both a complexing agent and a reducing agent. However, also in this case, the obtained silver particles have a wide particle diameter distribution.

[0009] In addition, Patent Literature 3 proposes a method for obtaining silver particles by forming a silver-amine complex using an alkoxyamine such as 3-methoxypropylamine. However, alkoxyamines have lower reducing power than that of alkanolamines, and it is necessary to further add another reducing agent. For this reason, particles having a wide particle size distribution are generated as in Patent Literature 2.

CITATION LIST

Patent Literature

[0010]

Patent Literature 1: Japanese Patent Application Publication No. 2004-346429
Patent Literature 2: Japanese Patent Application Publication No. H7-76710
Patent Literature 3: Japanese Patent Application Publication No. 2016-164312

SUMMARY

Problems to be solved

[0011] The present invention has been made in view of the above problems and circumstances, and its object to be achieved is to provide a method for producing silver nanoparticles having high monodispersity.

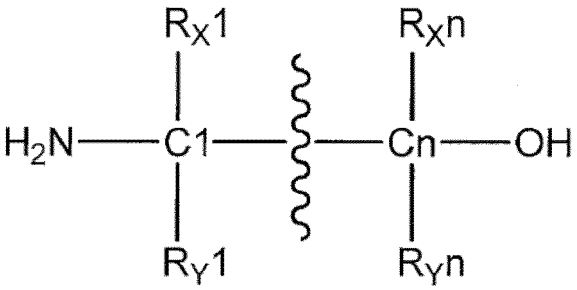
Means for Solving Problems

[0012] The above problem according to the present invention is solved by the following means.

1. A method for producing silver nanoparticles, comprising the steps of: forming a silver-amine complex as a precursor by reacting a silver compound with an amine compound in the presence of a dispersant; and precipitating a silver nanoparticle from a chemical reaction system containing the silver-amine complex, wherein the amine compound contains at least one compound represented by the following chemical formula (1):

[Chem. 1]

[Chemical Formula (1)]



(where n is an integer of 2 to 10, each R_X and R_Y is independently a hydrogen, an aliphatic or alicyclic alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 20 carbon atoms, an aralkyl group as a mixture thereof, an alkyl group with a substituted functional group, an aryl group with a substituted functional group or a heterocyclic compound with a substituted functional group, and each R_X and R_Y above is independently allowed to form a ring via connecting with an alkylene containing or not containing a hetero atom).

2. The method for producing a silver nanoparticle according to 1 described above, wherein n in the chemical formula (1) is two to four.

3. The method for producing a silver nanoparticle according to 1 or 2 described above, wherein each Rx and Ry in the chemical formula (1) is independently hydrogen, a methyl group, or an ethyl group.

4. The method for producing a silver nanoparticle according to any one of 1 to 3 described above, wherein the amine compound in the chemical formula (1) has 3 or more carbon atoms.

5. The method for producing a silver nanoparticle according to any one of 1 to 4 described above, wherein the amine compound in the chemical formula (1) is at least one of 3-amino-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-butanol, and 2-amino-1-butanol.

6. The method for producing a silver nanoparticle according to any one of 1 to 5 described above, wherein the dispersant is a polymer-based dispersant.

7. The method for producing a silver nanoparticle according to any one of 1 to 6 described above, wherein the chemical reaction system containing the silver-amine complex is performed in a temperature range between 20°C to 100°C.

8. The method for producing a silver nanoparticle according to any one of 1 to 7 described above, wherein the silver compound is silver nitrate, silver oxide, or silver carbonate.

9. The method for producing silver nanoparticles according to any one of 1 to 8 described above, further comprising a washing step after the step of precipitating the silver nanoparticles.

Advantageous Effects of Invention

[0013] The present invention provides a method for producing silver nanoparticles having high monodispersity.

BRIEF DESCRIPTION OF DRAWINGS

[0014]

FIG. 1 is a flowchart of a method for producing silver nanoparticles in an embodiment.
FIG. 2 is a flowchart of a method for producing silver nanoparticles in another embodiment.
FIG. 3 is an image of silver nanoparticles of No. 1 in Examples.
FIG. 4 is an image of silver nanoparticles of No. 11 in Examples.

EMBODIMENTS FOR CARRYING OUT INVENTION

[0015] Hereinafter, embodiments are described in detail. Note that the embodiments described below exemplify a method for producing a silver nanoparticle for embodying the technical idea of the present embodiment, and are not limited to the following. Note that, in the present application, "to" indicating a numerical range is used to mean that the numerical values written before and after it are included as the lower limit and the upper limit.

«Method for Producing Silver Nanoparticles»

[0016] As illustrated in FIG. 1, the method for producing silver nanoparticles of the present embodiment includes a step S101 of forming a silver-amine complex and a step S102 of precipitating a silver nanoparticle.

[Step of Forming Silver-Amine Complex]

[0017] The step S101 of forming a silver-amine complex is a step of forming a silver-amine complex as a precursor by reacting a silver compound with an amine compound in the presence of a dispersant.

[0018] The dispersant is not particularly limited, but is preferably a polymer-based dispersant. By using a polymer-based dispersant, particles are less likely to aggregate.

[0019] Examples of the dispersant include the following.

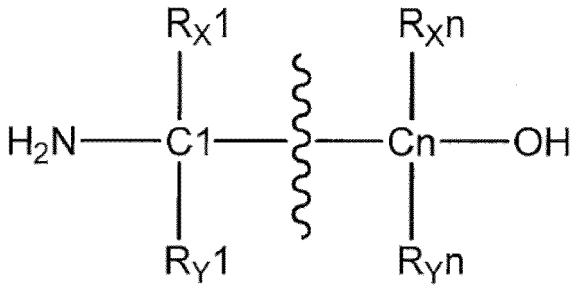
[0020] Examples of the SOLSPERSE (registered trademark) series manufactured by Lubrizol include SOLSPERSE-16000, 21000, 41000, 41090, 43000, 44000, 46000, and 54000. Examples of the DISPERBYK (registered trademark) series manufactured by BYK-Chemie include DISPERBYK-102, 110, 111, 170, 190, 194N, 2015, 2090, and 2096. Examples of the TEGO Dispers series manufactured by Evonik include 610, 610S, 630, 651, 655, 750W, and 755W. Examples of the Disparlon (registered trademark) series manufactured by Kusumoto Chemicals, Ltd. include DA-375 and DA-1200. Examples of the Floren series manufactured by Kyoei Kagaku Kogyo include WK-13E, G-700, G-900, GW-1500, GW-1640, and WK-13E. The dispersant may be used alone or in a combination of two or more kinds.

[0021] Examples of the silver compound include silver salts such as silver nitrate, silver sulfate, silver chloride, silver oxide, silver nitrite, silver chlorate, silver sulfide, and silver carbonate. These are not particularly limited as long as they are reduced, and may be dissolved in an appropriate solvent or used while being dispersed in the solvent. In addition, these may be used alone or in a combination of two or more kinds.

[0022] The silver compound is more preferably silver nitrate, silver oxide, or silver carbonate, and further preferably silver nitrate. The use of these silver compounds allows the amine compound to coordinate with silver more easily.

[0023] The amine compound contains at least one compound represented by the following chemical formula (1).

[Chem. 2]



[0024] In the formula, n is an integer of 2 to 10.

[0025] Each R_X and R_Y is independently a hydrogen, an aliphatic alkyl group having 1 to 30 carbon atoms, alicyclic

alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 20 carbon atoms, an aralkyl group as a mixture thereof, an alkyl group with a substituted functional group, an aryl group with a substituted functional group or a heterocyclic compound with a substituted functional group.

[0026] Note that the aralkyl group as a mixture thereof means an aralkyl group having a mixed structure of an aryl group having 6 to 20 carbon atoms and any one of an aliphatic alkyl group having 1 to 30 carbon atoms and an alicyclic alkyl group having 1 to 30 carbon atoms.

[0027] Each R_X and R_Y may be independently connected with an alkylene containing or not containing a hetero atom to form a ring. The alkylene may contain a heteroatom but also not contain a heteroatom.

[0028] Note that, from the viewpoint of further improving the adsorptivity of the amino group to silver, the hetero atom is preferably not a substituent possibly preventing the adsorption of the amino group to silver (SH, COOH, NH).

[0029] In addition, in the formula, the number 1 in C1, R_X1, and R_Y1 means the first structure, and the wavy line indicates that the first to n-th structures are bonded. In other words, the chemical formula (1) has a structure in which NH_2 is located at one end and OH at the other end, and 1 to n pieces of a structure composed of C, R_X, and R_Y are bonded.

[0030] Moreover, in a case where n = 4 in the chemical formula (1) as an example, a site composed of C1, R_X1 and R_Y1, a site composed of C2, R_X2 and R_Y2, a site composed of C3, R_X3 and R_Y3, and a site composed of C4, R_X4 and Ry4 are independent respectively. That is, for example when n = 4, R_X1, R_Y1 and R_X2 may be methyl groups, and R_Y2, R_X3, R_Y3, R_X4 and R_Y4 may be a hydrogen.

[0031] In the present embodiment, particle diameters of the silver nanoparticles are controlled by the adsorption of the amine compound represented by the chemical formula (1) to the silver compound. This increases the monodispersity of the silver nanoparticles.

[0032] In the chemical formula (1), n is preferably 2 to 4. The detailed mechanism is unknown, but is speculated as follows. When n is in this range, the bond distance between the terminal hydroxy moiety and the amino group becomes shorter, the hydroxy moiety is not separated from the silver surface while amino group is being adsorbed to the silver and the adsorptivity is improved. As a result, the amino group or hydroxy group is adsorbed to the silver surface produced immediately after the reduction of silver, whereby aggregation at the initial stage of particle production is reduced and particles having high monodispersity are produced.

[0033] In addition, when n is 5 or more, the bond distance between the terminal hydroxy moiety and the amino group becomes longer, and the degree of freedom of the main chain increases while the amino group is being adsorbed to silver. Therefore, the hydroxy moiety is easily separated from the silver surface. As a result, particles having low monodispersity are produced as compared with the case where n is 2 to 4.

[0034] Further, alkanolamines exhibit good reducibility on silver, whereas alkoxyamines without hydroxy groups exhibit little reducibility. Moreover, even when 3-methoxypropylamine, which is an alkoxyamine, is mixed with a compound having a hydroxy group such as ethanol, the reducibility on silver is not improved. This suggests that the hydroxy groups in alkanolamines have a strong effect on the reducibility on silver. Therefore, whether hydroxy groups are close to silver greatly affects not only monodispersity but also reducibility.

[0035] R_X and R_Y in the chemical formula (1) are preferably short substituents, and each of them is preferably a hydrogen, a methyl group, or an ethyl group, independently. With these substituents, steric hindrance is small, coordination of the amine moiety to silver is not prevented, and complexation is facilitated. In addition, the hydroxy moiety likely becomes closer to silver, so that the monodispersity is improved and the reducibility is likely exhibited.

[0036] The number of carbon atoms contained in the amine compound in the chemical formula (1) is preferably 3 or more. The detailed mechanism is unknown, but is speculated as follows. When n = 3 or more, the hydroxy moiety is likely closer to silver. As a result, the amino group or hydroxy group is adsorbed to the silver surface produced immediately after the reduction of silver, whereby aggregation at the initial stage of particle production is prevented and particles having high monodispersity are produced (example: 3-amino-1-propanol and the like).

[0037] In addition, in a case where n = 2 and the structure has a methyl group or the like as a substituent, it is speculated that the electron donicity and steric hindrance of the substituent increase the reducibility (example: 2-amino-2-methyl-1-propanol) although the detailed mechanism is unknown.

[0038] Meanwhile, the number of carbon atoms contained in the amine compound in the chemical formula (1) is preferably 20 or less from the viewpoint of adsorption of the hydroxy moiety to silver. When the number of carbon atoms is 20 or less, the bond distance between the terminal hydroxy moiety and the amino group becomes shorter, and the hydroxy moiety is not separated from the silver surface, so that the adsorptivity is improved. Therefore, particles having high monodispersity tend to be produced. In addition, when a large number of substituents are introduced to the positions of R in the side chains, a situation does not occur that the hydroxyl moiety or amino group is less likely adsorbed to silver due to the steric hindrance of the side chains. Thus, the adsorption to silver is facilitated.

[0039] Specific examples of the amine compound in the chemical formula (1) include 2-aminoethanol, 1-amino-2-propanol, 2-amino-2-methyl-1-propanol, 3-amino-2-methyl-2-butanol, 3-amino-2,3-dimethylbutan-2-ol,, 2-amino-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-1-butanol, 2-amino-1-pentanol, 2-aminocyclohexanol, 3-amino-1,2-propanediol, (3-aminooxolan-3-yl) methanol, 3- amino-1-propanol, 4-amino-2-butanol, 3-amino-1-butanol, 3-amino-2-me-

thyl-1-propanol, 4-aminopentan-2-ol, 3-aminocyclobutanol, 3-amino-4-methylpentan-1-ol, (2-aminocyclopentyl) methanol, 3-amino-3-methylbutan-1-ol, 2-(1-aminocyclopropyl) ethan-1-ol, 4-amino-4-methyl-pentan-2-ol, 4-amino-2-methyl-2-butanol, 1-(2-aminoethyl) cyclobutan-1-ol, 4-amino-1,2-butanediol, 4-amino-1-butanol, 4-amino-1-pentanol, 4-amino-2-methyl-1-butanol, 5-amino-2-methyl-2-pentanol, 4- aminocyclohexanol, 3-(aminomethyl) cyclobutanol, 3-hydroxy-3-methylcyclobutane-1-methamine, 3-(aminomethyl) cyclohexanol, 5-amino-1-pentanol, 5-amino-2,2-dimethylpentanol, 6-amino-1-hexanol, 4-(2-aminoethyl) cyclohexanol, 6-amino-2-hydroxymethyl hexan-1-ol, 8-amino-1-octanol, and 10-amino-1-decanol. These compounds result in particles having higher monodispersity. These compounds may be used alone or in a combination of two or more kinds.

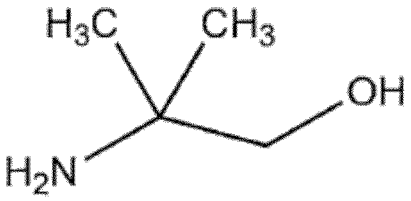
[0040] Among these, the amine compound in the chemical formula (1) is more preferably 3-amino-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-butanol, and 2-amino-1-butanol from the viewpoint of further improving monodispersity.

[0041] Presented below are 3-amino-1-propanol (formula (1-1)), 2-amino-2-methyl-1-propanol (formula (1-2)), 2-amino-1-propanol (formula (1-3)), 1-amino-2-propanol (formula (1-4)), 4-amino-1-butanol (formula (1-5)), and 2-amino-1-butanol (formula (1-6)).

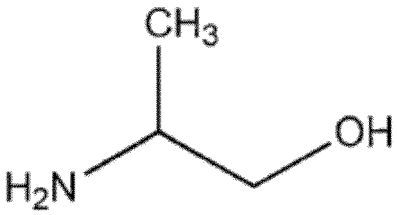
[Chem. 3]

Formula (1-1)

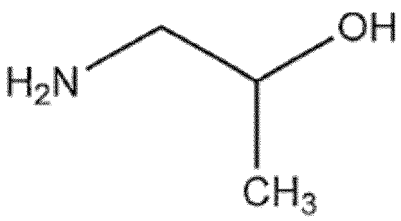
Formula (1-2)



Formula (1-3)

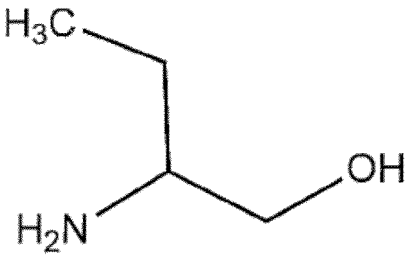


Formula (1-4)



Formula (1-5)

Formula (1-6)



[0042] The amine compound is acceptable when it contains at least one of the compounds represented by the chemical formula (1), and a trace amount of other amine compound other than the compounds represented by the chemical formula (1) may be contained as the amine compound in the chemical formula (1). However, from the viewpoint of further improving the monodispersity, the all amine compounds used are preferably compounds represented by the chemical formula (1).

[0043] Here, a trace amount of other amine compounds may be contained as long as a desired effect in the present invention is obtained. Specifically, the other amine compounds may be contained in an amount of, for example, 1 to 20% by mass in the entire amine compounds. Examples of the other amine compounds include tertiary amines such as triethanolamine. This is because tertiary amines have a low adsorptivity to silver and do not compete with the formation of the silver complex of the amine of the chemical formula (1).

[0044] The step of forming a silver-amine complex is performed, for example, as follows.

[0045] First, a dispersant is dissolved in ion exchange water. Next, silver nitrate dissolved in ion exchange water is added to the solution having the dispersant dissolved therein while being stirred. Next, an amine compound is added to the solution having silver nitrate added thereto, followed by stirring. As a result, a silver-amine complex is formed.

[0046] The amount of amine compound added is preferably 2 or more in terms of molar ratio to silver. In the case of 2 or more in molar ratio, complexation is performed. The amount of amine compound added is more preferably 2.5 or more, and further preferably 3 or more in terms of molar ratio to silver, from the viewpoint of facilitating complexation. On the other hand, the amount of amine compound added is preferably 6 or less in terms of molar ratio to silver, from the viewpoint of easiness of purification and economical efficiency.

[0047] In addition, preferably, the silver compound is 10 to 500 g, the amine compound is 10 to 1000 g, and the dispersant is 1 to 100 g per liter of water.

[Step of Precipitating Silver Nanoparticles]

[0048] The step S102 of precipitating silver nanoparticles is a step of precipitating silver nanoparticles from a chemical reaction system containing the silver-amine complex.

[0049] In this step, the chemical reaction system containing the silver-amine complex is preferably performed in a temperature range between 20 to 100°C. That is, it is preferable to heat the solution containing the silver-amine complex at 20 to 100°C.

[0050] When the reaction temperature is 20°C or more, the reaction is further promoted. In addition, for example, at about 20 to 30°C, the reaction may be performed even at around room temperature, so that the step is performed in a simple manner. Meanwhile, when the reaction temperature is 100°C or less, an aqueous solvent may be used as the solvent. In addition, economical efficiency is improved.

[0051] The reaction temperature is more preferably 30°C or more, and further preferably 40°C or more from the viewpoint of further promoting the reaction, and more preferably 90°C or less, and further preferably 80°C or less from the viewpoint of economical efficiency.

[0052] The reaction time is preferably 1 to 24 hours. When the reaction time is 1 hour or more, the reaction is further promoted. Meanwhile, when the reaction time is 24 hours or less, economical efficiency is improved.

[0053] The reaction time is more preferably 2 hours or more, and further preferably 3 hours or more from the viewpoint

of further promoting the reaction, and more preferably 15 hours or less, and further preferably 10 hours or less from the viewpoint of economical efficiency.

[0054] The step of precipitating silver nanoparticles is performed, for example, as follows.

[0055] First, a solution containing a silver-amine complex is heated to a predetermined temperature while being stirred. Next, the solution having reached the predetermined temperature is kept being stirred for a predetermined time while the temperature is maintained. Thereby, silver nanoparticles are precipitated and a reaction solution containing silver nanoparticles is obtained.

[0056] As another embodiment, as illustrated in FIG. 2, the step S102 of precipitating silver nanoparticles may be followed by a washing step S103.

[Washing Step]

[0057] The washing step S103 is a step of obtaining a silver nanoparticle dispersion solution by filtering the reaction solution containing silver nanoparticles, after the step S 102 of precipitating silver nanoparticles.

[0058] The washing step is performed, for example, as follows.

[0059] First, a reaction solution containing silver nanoparticles is placed in a stainless steel cup, ion exchange water is added to the solution and then the solution undergoes ultrafiltration. When the solution in the stainless steel cup decreases, ion exchange water is added again, and purification is repeated until the conductivity of the filtrate is equal to or lower than a predetermined value. After that, the filtrate is concentrated to obtain a silver nanoparticle dispersion solution.

[0060] The monodispersity of the silver nanoparticles obtained by the production method of the present invention is indicated by a coefficient of variation (CV) of the particle diameters and the CV value is preferably 25 or less. When the CV value is 25 or less, silver nanoparticles having better optical characteristic are obtained. The CV value is more preferably 20 or less, and further preferably 15 or less, from the viewpoint of obtaining better optical characteristics. Note that the lower the CV value is, the more preferable it is, so the lower limit thereof is not particularly specified.

[0061] Note that the CV value may be controlled by the type of the amine compound, the number of carbon atoms contained in the amine compound, and the like.

[0062] The CV value is calculated by the following formula (CV) using the values of the standard deviation and the average particle diameter in the number-based particle size distribution.

$$\text{CV value (\%)} = ((\text{standard deviation})/(\text{average particle diameter})) \times 100$$

[0063] Here, the standard deviation in the present application is calculated by the following formula, which is a known formula. In the following formula, n is actual measured counts, X_i is i-th actual measured data, and m is average value of actual measured data."

[Math. 1]

$$\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - m)^2}$$

[0064] Although the method for producing silver nanoparticles according to the present embodiment is as described above, the method may include another step during or before and after the above-described steps as long as the steps are not adversely affected. For example, the method may include a foreign matter removing step of removing foreign matter mixed during the production.

[0065] In addition, in the above-described steps, conventionally known conditions may be used for undescribed conditions, and it goes without saying that the conditions may be appropriately changed as long as the effects obtained by the processes the above-described steps are exhibited.

EXAMPLES

[0066] Hereinafter, the present invention is described specifically with reference to examples, but the present invention is not limited thereto.

[No. 1]

[0067] 8.4 g of DISPERBYK-190 and 295 g of ion exchanged water were put into a 1 L separable flask with a plate-shaped stirring blade and baffle and the DISPERBYK-190 was dissolved by stirring. Subsequently, 70 g of silver nitrate dissolved in 295 g of ion exchange water was added to the separable flask with stirring. Furthermore, 93 g of 3-amino-1-propanol (3 equivalents in terms of molar ratio to silver) was added to the mixture and stirred. Thereafter, the separable flask was placed in a water bath and heated with stirring until the temperature of the solution became stable at 50°C. Furthermore, stirring was continued for 3 hours while the temperature of the solution was maintained at 50°C to obtain a reaction solution containing silver nanoparticles.

[0068] The resultant reaction solution was put in a stainless steel cup, 2 L of ion exchange water was further added thereto, and then a pump was operated to perform ultrafiltration. When the solution in the stainless steel cup decreased, ion exchange water was added to it again, and purification was repeated until the conductivity of the filtrate was 100 μS/cm or less. After that, the filtrate was concentrated to obtain a silver nanoparticle dispersion solution having a solid content of 30% by mass.

[0069] Note that the ultrafiltration apparatus used was an ultrafiltration module AHP 1010 (manufactured by Asahi Kasei Corporation, molecular weight cutoff: 50000, number of membranes used: 400) connected to a tube pump (manufactured by Masterflex) via Tygon tubing.

(Evaluation of Monodispersity)

[0070] The average particle diameter of the silver nanoparticles in the resultant solution was calculated, and the CV value was also calculated as an index of monodispersity.

[0071] Specifically, the particle diameter was observed by SEM, image processing software ImageJ (version 1.49) was used to measure 100 particles, and these values were used to calculate the average particle diameter and CV value. Then, those having a CV value of 25 or less were evaluated as having excellent monodispersity.

[0072] Note that The CV value was specifically determined as follows.

$$\text{CV value (\%)} = ((\text{standard deviation})/(\text{average particle diameter})) \times 100$$

[Nos. 2 to 13]

[0073] Silver nanoparticles were synthesized in the same manner as in No. 1, in which only the amine compound used is changed. Note that the amount of the amine compound added was set to 3 equivalents in terms of molar ratio to silver as in No. 1.

[0074] Evaluation of monodispersity was performed in the same manner as in No. 1.

[0075] Table 1 presents the results. In the table,"-" means that measurement was impossible. FIG. 3 illustrates an image of the silver nanoparticles of No. 1, and FIG. 4 illustrates an image of the silver nanoparticles of No. 11.

[Table 1]

No.	Amine Compound as Reducing Agent and Complexing Agent			Average Particle Diameter (nm)	CV Value
	Compound	Amine Type	Number of Carbon Atoms		
1	3-Amino-1-Propanol	Primary Amine	3	35	13
2	2-Amino-2-Methyl-1-Propanol	Primary Amine	4	30	14
3	2-Aminoethanol	Primary Amine	2	38	21
4	2-Amino-1-Propanol	Primary Amine	3	32	15
5	1-Amino-2-Propanol	Primary Amine	3	34	14
6	4-Amino-1-Butanol	Primary Amine	4	36	15

(continued)

No.	Amine Compound as Reducing Agent and Complexing Agent			Average Particle Diameter (nm)	CV Value
	Compound	Amine Type	Number of Carbon Atoms		
7	2-Amino-1-Butanol	Primary Amine	4	32	15
8	4-Amino-2-Methyl-1-Butanol	Primary Amine	5	35	17
9	5-Amino-1-Pentanol	Primary Amine	5	38	20
10	6-Amino-1-Hexanol	Primary Amine	6	41	21
11	Dimethylaminoethanol	Tertiary Amine	4	52	27
12	Diethanolamine	Secondary Amine	4	43	28
13	3-Methoxypropylamine	Primary Amine	3	-	-

[0076] As illustrated in Table 1, Nos. 1 to 10, which were Examples satisfying the requirements of the present invention, were low in CV value and excellent in monodispersity.

[0077] In particular, Nos. 1 and 2 as well as Nos. 4 to 7 have lower CV values respectively because they used preferable amine compounds, 3-amino-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-butanol, and 2-amino-1-butanol.

[0078] In addition, No. 3 has a somewhat high CV value because of a small number of carbon atoms. In addition, No. 9 and No. 10 have somewhat high CV values because of a large number of carbon atoms between the amino group and the hydroxy group.

[0079] On the other hand, Nos. 11 to 13, which were Comparative Examples not satisfying the requirements of the present invention, provided the following results.

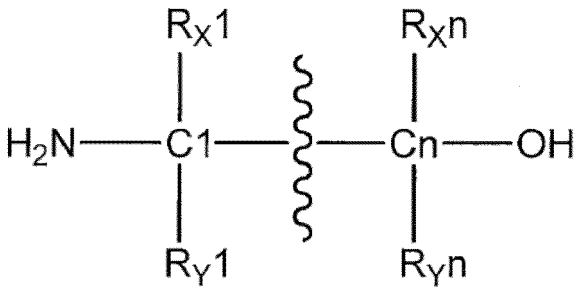
[0080] Nos. 11 and 12 have high CV values and inferior in monodispersity because they used compounds not satisfying the chemical formula (1) as the amine compounds.

[0081] No. 13 used an alkoxyamine compound corresponding to a primary amine but having no hydroxy group, and did not satisfy the chemical formula (1). The alkoxyamine compound has lower reducing power than that of the hydroxyamine compound, and silver nanoparticles could not be obtained.

Claims

1. A method for producing silver nanoparticles, comprising the steps of: forming a silver-amine complex as a precursor by reacting a silver compound with an amine compound in the presence of a dispersant; and precipitating a silver nanoparticle from a chemical reaction system containing the silver-amine complex, wherein the amine compound contains at least one compound represented by the following chemical formula (1):

[Chemical Formula (1)]



(where n is an integer of 2 to 10, each of R_X and R_Y is independently a hydrogen, an aliphatic or alicyclic alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 20 carbon atoms, an aralkyl group as a mixture thereof, an alkyl group with a substituted functional group, an aryl group with a substituted functional group, or a heterocyclic

compound with a substituted functional group, and each of R_X and R_Y above is independently allowed to form a ring via connecting with an alkylene containing or not containing a hetero atom.

2. The method as claimed in claim 1, wherein n in the chemical formula (1) is two to four.

3. The method as claimed in claim 1 or 2, wherein each R_X and R_Y in the chemical formula (1) is independently hydrogen, a methyl group, or an ethyl group.

4. The method as claimed in any one of claims 1 to 3, wherein the amine compound in the chemical formula (1) has three or more carbon atoms.

5. The method as claimed in any one of claims 1 to 4, wherein the amine compound in the chemical formula (1) is at least one of 3-amino-1-propanol, 2-amino-2-methyl-1-propanol, 2-amino-1-propanol, 1-amino-2-propanol, 4-amino-1-butanol, and 2-amino-1-butanol.

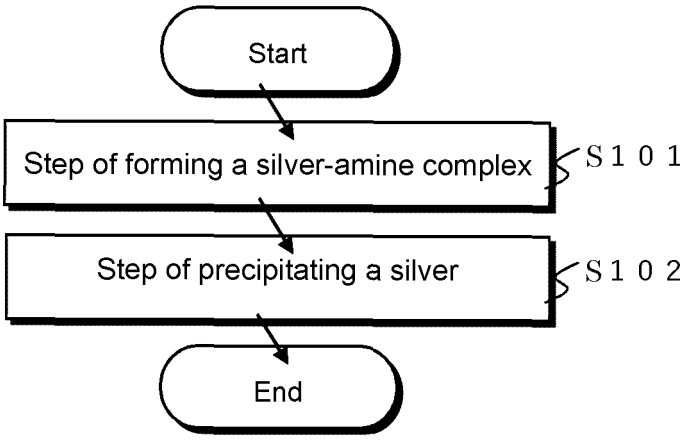
6. The method as claimed in any one of claims 1 to 5, wherein the dispersant is a polymer-based dispersant.

7. The method as claimed in any one of claims 1 to 6, wherein the chemical reaction system containing the silver-amine complex is performed in a temperature range between 20°C to 100°C.

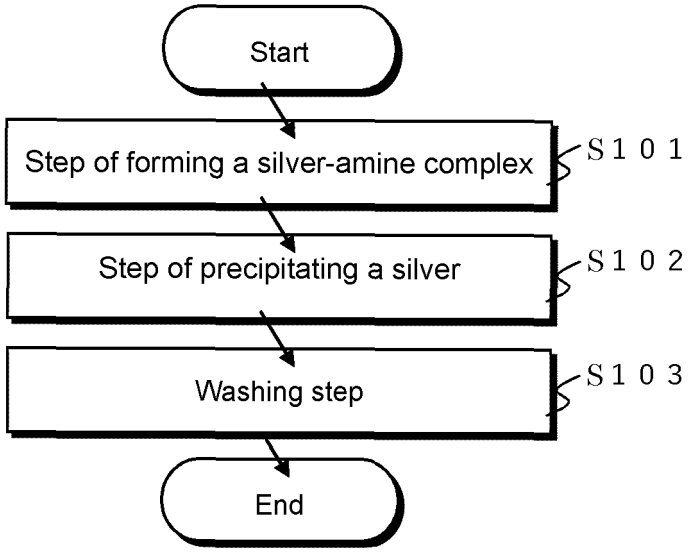
8. The method as claimed in any one of claims 1 to 7, wherein the silver compound is silver nitrate, silver oxide, or silver carbonate.

9. The method as claimed in any one of claims 1 to 8, comprising a washing step after the step of precipitating the silver nanoparticles.

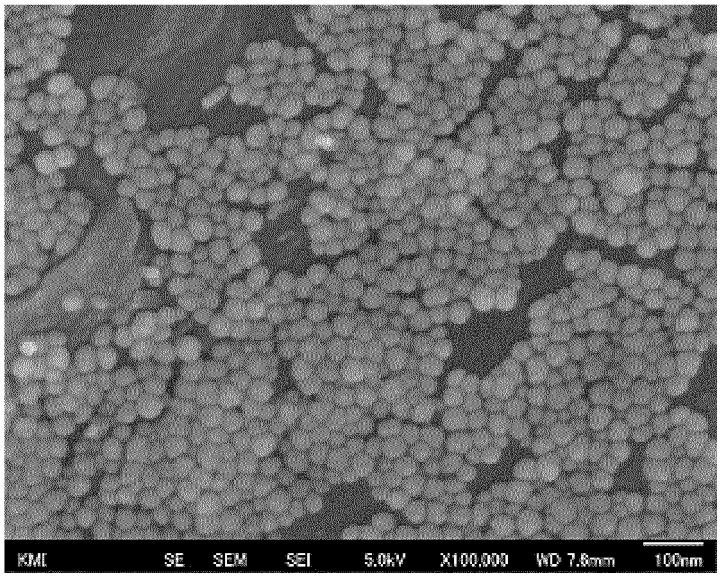
【Fig.1】


Start
Step of forming a silver-amine complex
S101
Step of precipitating a silver
S102
End

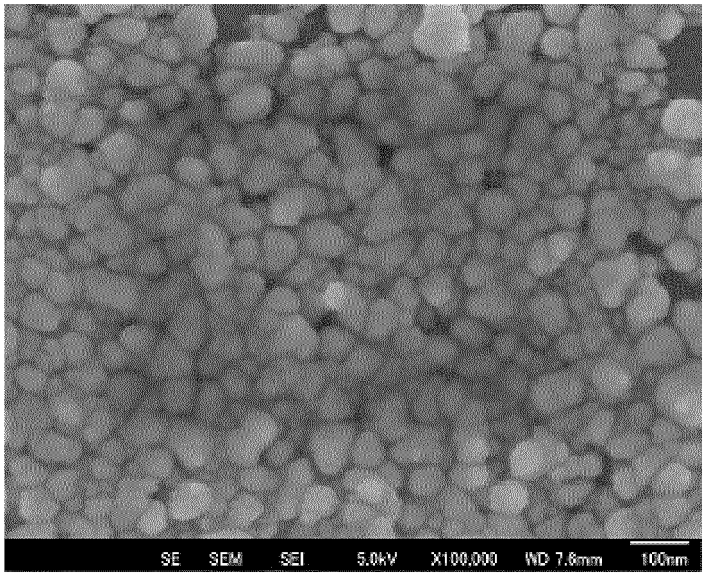
【Fig.2】


Start
Step of forming a silver-amine complex
S101
Step of precipitating a silver
S102
Washing step
S103
End

【Fig.3】



【Fig.4】



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/037573

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. B22F9/24(2006.01)i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. B22F9/24

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2018
Registered utility model specifications of Japan	1996-2018
Published registered utility model applications of Japan	1994-2018

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/155134 A1 (NIPPON SHEET GLASS CO., LTD.) 15 December 2011, paragraphs [0002]-[0003], [0032]-[0050] & US 2013/0069017 A1, paragraphs [0002]-[0010], [0055]-[0075] & EP 2581153 A1 & CN 102933336 A	1-9
A	JP 2005-325374 A (HITACHI CHEMICAL INDUSTRY CO., LTD.) 24 November 2005, entire text, fig. 1-2 (Family: none)	1-9

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 December 2018 (11.12.2018)	25 December 2018 (25.12.2018)

Name and mailing address of the ISA/	Authorized officer
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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2004346429 A **[0010]**
- JP H776710 B **[0010]**
- JP 2016164312 A **[0010]**