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(54) METHOD FOR PRODUCING FINE PARTICLES OF SILVER

(57) The present application provides a method of producing silver fine particles, comprising continuously reducing silver ions contained in a silver compound to precipitate silver fine particles by introducing at least two fluids from separate flow paths and mixing the fluids, wherein one fluid of the at least two fluids contains the silver compound, and another fluid contains a reducing agent, and at least one fluid of the at least two fluids contains an amino acid. By the present invention, silver fine particles can be produced with sufficient continuous productivity and quality uniformity, without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia.

Processed by Luminess, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a method of producing silver fine particles.

BACKGROUND ART

[0002] In recent years, improvement of the patterning technology for conductive members has been required in applications such as solar cells, displays and sensors. Since silver exhibits high conductivity and oxidation resistance, it is widely used as a conductive material for wiring, electrodes, and the like. In order to achieve microfabrication of wiring and electrodes, silver fine particles used in a paste agent for forming wiring and electrodes are required to have an appropriately small particle diameter, and particularly to have a uniform particle diameter. Further, production of silver fine particles is required to have high productivity from the viewpoint of economy.

[0003] As a method of producing silver fine particles for a paste agent for wiring and electrode formation, a wet reduction method of reducing silver ions by a chemical method (a liquid phase reduction method) is mainly used. As a method of producing silver fine particles by this wet reduction method, Patent Literature 1 discloses a method of producing silver fine particles by reducing a raw material solution containing a silver compound with a reducing agent, while a cationic surfactant is added to the reaction solution. However, when the wet reduction method is performed in a batch system as in Patent Literature 1, it is difficult to obtain uniform silver fine particles because the reaction field is non-uniform due to the temperature gradient and the concentration gradient in the batch system.

[0004] In order to solve this problem, Patent Literatures 2 and 3 discloses a method of producing silver fine particles by the wet reduction method using a continuous reactor, comprising flowing a fluid containing a silver compound into one of the two flow paths and a fluid containing a reducing agent into the other, bringing the two fluids into contact with each other at the merging portion of the two flow paths, and mixing the two fluids to precipitate silver fine particles. By merging the two flow paths, the mixing of the two fluids is completed in a short time, and the reaction proceeds in a uniform state in the system, so that silver fine particles having a uniform shape and properties are produced. Further, unlike the batch type system using a conventional reaction vessel, silver fine particles can be continuously produced, which is advantageous from the viewpoint of productivity.

[0005] On the other hand, electroless plating technology is widely used. Silver mirror reaction is classified into a reduced non-catalytic type of the electroless plating technology, in which a silver salt solution and a reducing agent are mixed to form silver plating on the surface of the obj ect to be plated. However, it is known that the reduction reaction in the silver mirror reaction proceeds not only on the surface of the object to be plated, but also on the wall surface of the plating bath vessel in the plating bath.

[0006] Therefore, also in the methods of producing silver fine particles of Patent Literatures 2 and 3, the reduction reaction proceeds not only in the reaction system, but also on the inner walls of the merging portion and the flow path of the downstream thereof, and silver also adheres to the surface of the inner walls of the merging portion and the flow path of the downstream thereof to form a silver mirror. When a silver mirror is formed on the inner wall of the merging portion and the flow path, there is a problem as follows. Since the silver compound is continuously introduced into the merging portion and the flow path, the amount of the adhered silver increases with lapse of time, and finally the adhered silver blocks the merging portion and the flow path. Therefore, it is necessary to regularly clean or replace the merging portion and the flow path, so that productivity of equipment is lowered.

[0007] To solve this problem, known is a method of using ammoniacal silver nitrate of an ammine complex obtained by adding ammonia to silver nitrate as a raw material solution. However, due to use of ammoniacal silver nitrate, ammonia odor is terrible and the working environment is very poor. Further, ammoniacal silver nitrate has a problem of generating explosive fulminating silver when it is left in contact with a reducing substance such as an alcohol. Thus, use of a large amount of ammonia should be avoided.

[0008] Patent Literature 4 describes a method of producing silver fine particles in the presence of sodium citrate. Citric acid may be a protective agent for silver. But, since the coordinating power of citric acid to a silver ion is weaker than that of ammonia, citric acid cannot sufficiently prevent the adhesion of silver in the continuous wet reduction method.

[0009] Patent Literatures 5 and 6 describe a method of producing silver fine particles by a wet reduction method using a continuous forced thin film reactor which mixes reaction fluids in a thin film fluid formed between at least two processing surfaces being capable of approaching to and separating from each other, at least one of which rotates relative to the other. In this method, self-discharging property of the forced thin film reactor can prevent blockage of the flow path by the product, and uniform fine particles can be efficiently produced.

[0010] However, in the case of silver fine particles, even if a forced thin film reactor is used, some silver inevitably precipitates on the inner wall surface of the merging portion and the flow path, so that the shape and surface material of the processing surfaces which constitute a reaction space change. As the shape and surface material the processing surfaces change, the shape and properties of the silver fine particles produced on the processing surfaces also change. Accordingly, in the case of continuously producing silver fine particles for mass-production of uniform silver fine particles, even if a forced thin film reactor is used, adhesion of silver onto the processing surfaces proceeds with lapse of time from the start of production, resulting in a problem that the shape and properties of the produced silver fine particles change. In particular, when a concentration of silver in the fluid containing a silver compound increases in order to pursue mass productivity, precipitation is more likely to occur, and the problem becomes even more serious.

CITATION LIST

PATENT LITERATURE

[0011]

Patent Literature 1: JP S61-243105
Patent Literature 2: JP 2005-048236
Patent Literature 3: JP 2010-070793
Patent Literature 4: JP 2006-045655
Patent Literature 5: WO 2009/008390
Patent Literature 6: WO 2012/165000
Patent Literature 7: JP 2019-108610
Patent Literature 8: JP 2011-021252

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0012] As described above, when silver fine particles are produced by a continuous wet reduction method using a continuous reactor such as a forced thin film reactor, silver inevitably precipitates on the inner wall surface of the merging portion and the flow path by the conventional production method. As a result, as the environment of the merging portion and the flow path changes with lapse of time, the shape and properties of the produced silver fine particles change unexpectedly. Therefore, it is extremely difficult to control the shape and properties of the silver fine particles in order to ensure the uniformity with respect to the elapsed time of the continuous processing, and there was a problem in quality control.

[0013] Therefore, the problem to be solved by the present invention is to solve these conventional problems, and to provide a method of producing silver fine particles in a wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia.

SOLUTION TO THE PROBLEM

[0014] As a result of diligent research, the present inventors have surprisingly found that in the production method of silver fine particles which continuously precipitates silver fine particles by a redox reaction by mixing a plurality of fluids flowing from separate flow paths, silver fine particles can be continuously, stably and uniformly produced by adding an amino acid to at least one of the plurality of fluids, while the adhesion of silver on the inner walls of the merging portion and the flow path of the downstream thereof is suppressed. Thus, the present invention has been accomplished.

[0015] An amino acid used in the present invention has two types of functional groups, an amino group and a carboxyl group, which can coordinate to a silver ion within the molecule. Amino acids are available in a powder form which is highly safe and easy to handle, so that they can be effectively used as a substitute for ammonia.

[0016] Patent Literature 7 discloses a method of producing silver fine particles for a conductive paste, which uses a neutral or basic amino acid having 5 or more carbon atoms. However, the production method is characterized in that a conductive film having a low volume resistivity can be formed by remaining the amino acid within the formed silver fine particles and sintering the silver fine particles at a relatively low temperature. The amino acid is not used as a complexing agent for a silver ion, but as an impurity remaining in silver fine particles. Further, in the examples, a silver ammine complex prepared from silver nitrate and aqueous ammonia is used as a raw material, and ammonia is used as a complexing agent for a silver ion. Therefore, the method still has the problems of ammonia odor and explosive fulminating silver as in the prior art.

[0017] Patent Literature 8 discloses a method of precipitating silver fine particles in an aqueous solution containing an amino acid and an aliphatic hydroxy acid metal salt. The method is characterized in that silver fine particles having a unique structure such as an X-letter shape or a flower-shape is produced, and therefor an amino acid is used to produce nuclei consisting of silver particles and the amino acid for forming one component (aggregate) having the specific shape. Further, in the examples, an aqueous reducing agent solution is added dropwise to and mixed with an aqueous mixed silver compound solution without stirring, and the mixture is stirred at a low speed even after the addition is completed. Therefore, the method of producing silver fine particles of Patent Literature 8 cannot be applied to a continuous wet reduction method in which a silver compound and a reducing agent are continuously and quantitatively mixed and reacted in a short time.

[0018] As described above, in Patent Literatures 7 and 8, amino acids are used in the production of silver fine particles. However, by the techniques of these Patent Literatures, silver fine particles cannot be produced in a wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, or without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia. Under such circumstances, the present invention solves the problem to be solved by the present invention, and provides a method of producing silver fine particles in a wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia.

[0019] The present invention is as follows.

1. The first embodiment of the present invention is a method of producing silver fine particles, comprising continuously reducing silver ions contained in a silver compound to precipitate silver fine particles by introducing at least two fluids from separate flow paths and mixing the fluids,

   wherein one fluid of the at least two fluids contains the silver compound, and another fluid contains a reducing agent, and
   at least one fluid of the at least two fluids contains an amino acid.

2. The second embodiment of the present invention is the method of producing silver fine particles according to the first embodiment, wherein formation of a silver mirror is suppressed by the amino acid.
3. The third embodiment of the present invention is the method of producing silver fine particles according to the first or second embodiment, wherein the amino acid is contained in the fluid containing the silver compound.
4. The fourth embodiment of the present invention is the method of producing silver fine particles according to any one of the first to third embodiments, wherein 0.1 to 4 mol of the amino acid is used with respect to 1 mol of the silver ion.
5. The fifth embodiment of the present invention is the method of producing silver fine particles according to any one of the first to fourth embodiments, wherein a concentration of the silver ion in the fluid containing the silver compound is 0.1 to 5% by mass.
6. The sixth embodiment of the present invention is the method of producing silver fine particles according to any one of the first to fifth embodiments, wherein a dispersing agent is contained in at least one fluid of the at least two fluids.
7. The seventh embodiment of the present invention is the method of producing silver fine particles according to any one of the first to sixth embodiments, wherein the amino acid is glycine.
8. The eighth embodiment of the present invention is the method of producing silver fine particles according to any one of the first to seventh embodiments, wherein the at least two fluids are mixed between at least two processing surfaces arranged so as to be capable of approaching to and separating from each other, at least one of which rotates relative to the other.
9. The ninth embodiment of the present invention is the method of producing silver fine particles according to any one of the first to eighth embodiments, wherein ammonia is not used.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0020] According to the method of producing silver fine particles of the present invention, silver does not adhere to the inner wall of the merging portion and the flow path of the continuous reactor in the continuous wet reduction method using the continuous reactor. Therefore, the environment of the merging portion and the flow path does not change with lapse of time, and the shape and properties of the produced silver fine particles can be controlled, and thus, silver fine particles with certain quality can be produced.

[0021] As described above, by the method of producing silver fine particles of the present invention, silver fine particles can be produced in a wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia.

DESCRIPTION OF THE INVENTION

[0022] Hereinafter, embodiments of the present invention are described in detail.

[0023] The method of producing silver fine particles of the present invention is a method of producing silver fine particles, comprising continuously reducing silver ions contained in a silver compound to precipitate silver fine particles by introducing at least two fluids from separate flow paths and mixing the fluids, wherein one fluid of the at least two fluids contains the silver compound, and another fluid contains a reducing agent, and at least one fluid of the at least two fluids contains an amino acid.

< Production apparatus of silver fine particles >

[0024] A production apparatus of the silver fine particles used in the present invention includes a continuous reactor having at least two flow paths and having a structure in which the flow paths are in contact with each other at the merging portion. The structure of the merging portion in the continuous reactor is not particularly limited. For example, a Y-letter shaped pipe passage, a T-letter shaped pipe passage, a coaxial double pipe passage, or the like can be used as the flow path that merges at the merging portion. Further, for the purpose of promoting mixing, a static mixer and an in-line mixer may be installed in the flow path of the downstream of the merging portion, or a mechanism for mechanically stirring may be provided at the merging portion. As the mechanism for mechanically stirring, a stirrer of various shear type, friction type, high pressure jet type, ultrasonic type and the like, or a dissolver, an emulsifier, a disperser, a pulverizer, a homogenizer and the like can be used. These continuous reactors include, for example, a continuous type emulsifier such as ULTRA-TURRAX (IKA Japan Co.Ltd.), HOMOMIXER (Primix Corporation), Milder (Pacific Machinery & Engineering, Co., Ltd.), HOMOMETIC LINE FLOW (Primix Corporation), Cavitron (Euro Tech, Co., Ltd.), Fine Flow Mill (Pacific Machinery & Engineering, Co., Ltd.) and the like; a pulverizer such as Slasher (NIPPON COKE & ENGINEERING, Co., Ltd.), Trigonal (Mitsui Miike Chemical Engineering Machinery, Co., Ltd.) and the like; a continuous stirrer such as Clearmix (M. Technique Co., Ltd.), Clearmix Dissolver (M. Technique Co., Ltd.), SWINGSTIR (Shinko Eco-Solutions Co., Ltd.), FILMIX (Primix Corporation), and the like.

< Forced thin film reactor >

[0025] A preferable embodiment of the production apparatus of silver fine particles used in the present invention includes, for example, a forced thin film reactor in which at least two types of fluids to be processed can be contacted and mixed with each other between at least two processing surfaces, at least one of which rotates relative to the other. More specifically, it may be a forced thin film reactor, wherein the reactor has the first processing surface and the second processing surface being capable of approaching to and separating from each other, at least one of which rotates relative to the other; at least two types of fluids to be processed are introduced between the at least two processing surfaces, and a separation force acting in the direction of separating the first processing surface and the second processing surface is generated by the pressure applied between the first processing surface and the second processing surface; a minute interval is maintained between the first processing surface and the second processing surface by the pressure balance with the pressure in the direction of bringing the processing surfaces closer to each other; a thin film fluid is formed by passing the at least two types of fluids to be processed between the first processing surface and the second processing surface kept at the minute interval; and the fluids to be processed are contacted and mixed with each other in the thin film fluid. Among them, a preferable forced thin film reactor used in the present invention has a mechanism for promoting mixing by relatively moving the processing surfaces while maintaining a constant interval at the mixing portion of the fluids to be processed. Specifically, for example, the forced thin film type fluid processing apparatus shown in JP 2010-189661 is preferably used.

< Silver compound >

[0026] The silver compound used in the present invention includes, for example, monovalent, divalent or trivalent silver compounds which can be dissolved in a solvent used in a fluid containing the silver compound, preferably monovalent silver compound. Specific examples of the silver compounds include silver nitrate, silver fluoride, silver sulfate, silver phosphate and the like, and more preferably silver nitrate. A concentration of silver ions in the fluid containing the silver compound is preferably, for example, 0.1% by mass or more in order to increase productivity. Further, it is preferably, for example, 5% by mass or less, because it becomes difficult to suppress formation of a silver mirror when a concentration of silver ions is too high. A concentration of silver ions is more preferably 0.5% by mass or more and 4.5% by mass or less, further preferably 1% by mass or more and 4% by mass or less, and even more preferably 1.5% by mass or more and 3% by mass or less.

< Reducing agent >

[0027] As the reducing agent used in the present invention, any reducing agent may be used, as long as it can reduce silver ions contained in the silver compound and precipitate silver fine particles. Preferred reducing agents include, for example, ascorbic acid, ferrous sulfate, sulfite, alkanolamine, formic acid, hydroquinone, glucose, formalin, sodium borohydride, hydrazine, a hydrazine compound (hydrazine sulfate, hydrazine chloride, etc.) and the like. Among these agents, for example, hydrazine, hydrazine compounds and the like are more preferable. The amount of the reducing agent used is preferably 1 equivalent or more, more preferably 1 equivalent or more and 20 equivalents or less, still more preferably 1.5 equivalents or more and 15 equivalents or less, and even more preferably 2 equivalents or more and 10 equivalents or less with respect to a silver ion in order to increase the reaction yield of silver fine particles. In the redox reaction, electrons are transferred between the compounds, and a silver ion receives one electron and is reduced to silver. A number of electrons transferred from one molecule differs for each of the above reducing agents. For example, hydrazine provides 4 electrons in the reduction reaction. Therefore, when hydrazine which transfers 4 electrons is a reducing agent, 1 equivalent or more with respect to a silver ion means 0.25 mol or more of hydrazine with respect to 1 mol of a silver ion. When a reducing agent having a weak reducing power is used, preferred are 2 equivalents or more, more preferably 2 equivalents or more and 50 equivalents or less, further preferably 5 equivalents or more and 30 equivalents or less, and even more preferably 10 equivalents or more and 20 equivalents or less with respect to a silver ion. A concentration of the reducing agent in the fluid containing the reducing agent is preferably, for example, 1% by mass or more in order to increase productivity. Further, a concentration is preferably, for example, 50% by mass or less, because silver fine particles become non-uniform when a concentration of the reducing agent is too high. A more preferable concentration of the reducing agent is 2.5% by mass or more and 40% by mass or less, and more preferably 5% by mass or more and 25% by mass or less.

< Amino acid >

[0028] The amino acid in the present invention has two types of functional groups: an amino group and a carboxyl group, which can be coordinated to a silver ion in the molecule. Therefore, a mixture of various types of complexes is formed, in which an amino group, a carboxyl group, or the like is coordinated to a silver ion. The amino acid stabilizes a silver ion by forming a mixture of silver ions and various types of complexes, and decrease the reduction rate immediately after mixing silver ions and the reducing agent, and thereby the formation of a silver mirror on the inner walls of the merging portion and the flow path of the continuous reactor is suppressed, and the adhesion of silver on the inner walls of the merging portion and the flow path is suppressed. In the present invention, it is preferable not to use a large amount of ammonia to some extent causing the problems of deterioration of working environment and generation of explosive fulminating silver. It is more preferable not to use ammonia.

[0029] The amino acid includes, for example, α-amino acid, β-amino acid, derivatives thereof and the like, and may be appropriately selected depending on the physical properties such as solubility and pKa. Preferred amino acids are, for example, α-amino acids. Specific α-amino acids include, for example, glycine, arginine, phenylalanine, glutamic acid, valine, leucine, isoleucine, glutamine, aspartic acid, alanine, proline, cysteine, lysine, threonine, asparagine, serine, methionine, tyrosine, histidine, tryptophan, citrulline, ornithine and the like. More preferable α-amino acids are glycine, arginine, phenylalanine, glutamic acid and the like. Specific β-amino acids and derivatives thereof are, for example, β-alanine, taurine, creatine and the like. The amino acid may be used alone or in combination of two or more. As for an amino acid in which optical isomers are present, any of D-form, L-form, or a mixture thereof may be used.

[0030] The amount of the amino acid added is preferably 5 mol or less with respect to 1 mol of a silver ion, because the progress of reduction is inhibited when the amount of the amino acid added is too large. Further, the amount of the amino acid added is preferably 0.05 mol or more with respect to 1 mol of a silver ion, because silver ions become unstable and the formation of a silver mirror cannot be suppressed when the amount of the amino acid added is too small. A more preferable amount of the amino acid added is, for example, 0.1 mol or more and 4 mol or less, and more preferably 0.2 mol or more and 2 mol or less with respect to 1 mol of a silver ion.

[0031] In the present invention, the amino acid is contained in at least one of at least two fluids introduced from separate flow paths. Preferably, the amino acid is contained in a fluid containing the silver compound. When both the amino acid and the silver compound are contained in the same fluid, the silver ion forms a stable complex with the amino acid and can be reacted with the reducing agent in the state of the complex. Not limited to this, the present invention also includes an embodiment in which a fluid containing the silver compound, a fluid containing the reducing agent, and a fluid containing the amino acid are introduced from separate flow paths and mixed.

< Solvent >

[0032] In the present invention, the solvent used in the fluid containing the silver compound or the reducing agent may be any solvent which can dissolve the silver compound or the reducing agent, and does not cause a problem in the reduction of a silver ion. Such solvent includes, for example, water, a hydrophilic solvent, and a mixed solvent thereof, and preferably water, and a mixed solvent of water and a hydrophilic solvent, and more preferably water. In order to avoid formation of silver chloride or the like, it is desirable to use desalted water, and specific examples thereof include ion-exchanged water, RO water (reverse osmosis water), pure water, and ultrapure water and the like. The hydrophilic solvent includes, for example, an alcohol such as methanol, ethanol and ethylene glycol; a ketone such as acetone and methyl isobutyl ketone; a sulfoxide such as dimethyl sulfoxide; an amide such as dimethylformamide and dimethylacetamide; an ether such as tetrahydrofuran, dioxane, dimethoxyethane and polyethylene glycol; a carboxylic acid such as acetic acid, and the like. Preferred is an alcohol such as methanol, ethanol and ethylene glycol. For example, a mixed solvent of water and a hydrophilic solvent is preferred, when water alone is insufficient to uniformly dissolve a dispersing agent or the like, or when water alone is insufficient to obtain the viscosity required for circulation in a flow path.

< Dispersing agent >

[0033] In the method of producing silver fine particles of the present invention, it is also preferable to add a dispersing agent. The dispersing agent is not particularly limited, and may be appropriately selected depending on the intended purpose. Examples thereof include a fatty acid and a salt thereof, a surfactant, an organometallic compound, a chelating agent, a polymer dispersing agent and the like. The fatty acid and a salt thereof include, for example, propionic acid, caprylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, arachidonic acid, ricinoleic acid and a salt thereof.

[0034] The surfactant includes, for example, an anionic surfactant such as an alkyl sulfonate and an alkylbenzene sulfonate; a cationic surfactant such as an alkylpyridinium salt and a quaternary alkylammonium salt; a nonionic surfactant such as a polyoxyethylene alkyl ether; or a mixture thereof and the like. Specific examples of the surfactant include Ajisper (registered trademark, Ajinomoto Fine Techno Co., Inc.), Hypermer (registered trademark, Croda International Plc.), Tween (registered trademark), Solplus (registered trademark, Lubrisol Japan Ltd.), SN Sparse (San Nopco Ltd.), Futagent (registered trademark, Neos Co., Ltd.), Beaulite (registered trademark, Sanyo Kasei Kogyo Co., Ltd.), Perex (registered trademark, Kao Co., Ltd.), Kaosera (registered trademark), Homogenol (registered trademark), Pluronic (registered trademark, BASF SE), Catiogen (registered trademark, Dai-Ichi Kogyo Seiyaku Co., Ltd.), Hitenol (registered trademark), Plysurf (registered trademark), Neugen (registered trademark), Epan (registered trademark), Sorgen (registered trademark), DK ester (registered trademark), Surfinol (registered trademark, Nisshin Kagaku Kogyo Co., Ltd.), Megafac (registered trademark, DIC Corporation), and the like. The organometallic compound include, for example, acetylacetone tributoxyzirconium, magnesium citrate, diethylzinc, dibutyltin oxide, dimethylzinc, tetra-n-butoxyzirconium, triethylindium, triethylgallium, trimethylindium, trimethylgallium, monobutyltin oxide, tetraisocyanatosilane, tetramethylsilane, tetramethoxysilane, monomethyltriisocyanatosilane, silane coupling agent, titanate-based coupling agent, aluminum-based coupling agent, and the like.

[0035] The chelating agent includes, for example, an azole compounds such as imidazole, oxazole, thiazole, selenazole, pyrazole, isoxazole, isothiazole, 1H-1,2,3-triazole, 2H-1,2,3-triazole, 1H-1,2,4-triazole, 4H-1,2,4-triazole, 1,2,3-oxadiazole, 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, 1,2,3-thiadiazole, 1,2,4-thiadiazole, 1,2,5-thiadiazole, 1,3,4-thiadiazole, 1H-1,2,3,4-tetrazole, 1,2,3,4-oxatriazole, 1,2,3,4-thiatriazole, 2H-1,2,3,4-tetrazole, 1,2,3,5-oxatriazole, 1,2,3,5-thiatriazole, indazole, benzoimidazole and benzotriazole, or a salt thereof; a dicarboxylic acid such as oxalic acid, succinic acid, malonic acid, glutaric acid and adipic acid, or a salt thereof; ethylenediamine tetraacetic acid, ethylenediamine-N,N'-disuccinic acid and the like.

[0036] Various polymer dispersing agents may be used. The polymer dispersing agent includes, for example, an amine-based polymer dispersing agent such as polyethyleneimine and polyvinylpyrrolidone; a hydrocarbon-based polymer dispersing agent having a carboxylic acid group in the molecule such as polyacrylic acid and carboxymethyl cellulose; Poval (polyvinyl alcohol); a polymer dispersing agent having a polar group such as a copolymer having a polyethyleneimine moiety and a polyethylene oxide moiety in one molecule, and the like. The polymer dispersing agent preferably has a molecular weight of 100,000 or less. Commercially available products may also be used, and examples of the commercially available products include Solsperse 20000, Solsperse 24000, Solsperse 26000, Solsperse 27000, Solsperse 28000, Solsperse 41000 (registered trademark, Nippon Lubrizol Co., Ltd.), and Disperbyk 160. , Disperbyk 161, Disperbyk 162, Disperbyk 163, Disperbyk 166, Disperbyk 170, Disperbyk 180, Disperbyk 181, Disperbyk 182, Disperbyk 183, Disperbyk 184, Disperbyk 190, Disperbyk 191, Disperbyk 192, Disperbyk 2000, Disperbyk 2001 (registered trademark, BYK Chemie Japan Co., Ltd.), Flowlen DOPA-158, Flowlen DOPA-22, Flowlen DOPA-17, Flowlen G-700, Flowlen TG-720W, Flowlen-730W, Flowlen-740W, Flowlen-745W (registered trademark, Kyoeisha Chemical Co., Ltd.), Ajisper PA111, Ajisper PB711, Ajisper PB811, Ajisper PB821, Ajisper PW911 (registered trademark, Ajinomoto Fine-Techno Co., Inc.), Joncryl 678, Joncryl 679, Joncryl 62 (registered trademark, by BASF SE) and the like.

[0037] These dispersing agents may be used alone or in combination of two or more.

[0038] In the present invention, the dispersing agent may be contained in at least one of at least two fluids introduced from separate flow paths. By containing the dispersing agent, the generated silver fine particles are stabilized, and the adhesion of silver on inner walls of the merging portion and the flow path is suppressed.

[0039] The amount of the dispersing agent added is preferably the amount that does not inhibit the coordination of the amino acid to a silver ion and does not adversely affect the effects of the present invention. The concentration of the dispersing agent in the fluid containing the dispersing agent is, for example, 0.0001% by mass or more and 1% by mass or less, preferably 0.0005% by mass or more and 0.5% by mass or less, more preferably 0.001% by mass or more and 0.1% by mass or less.

< pH adjusting agent >

[0040] A pH adjusting agent may be added as necessary to adjust difference in acidity derived from the raw material. As the pH adjusting agent, general acids and bases may be used. Examples thereof include nitric acid, sodium hydroxide, and the like.

< Reaction temperature >

[0041] In the method of producing silver fine particles of the present invention, the reaction temperature of the reaction in which silver ions contained in a silver compound are continuously reduced by introducing at least two fluids from separate flow paths and mixing, may be a temperature at which the solvent used does not solidify or vaporize. Preferred reaction temperature includes, for example, 5°C or higher and 80°C or lower, more preferably 10°C or higher and 60°C or lower, further preferably 15°C or higher and 50°C or lower, and even more preferably 20°C or higher and 40°C or lower.

EXAMPLE

[0042] Hereinafter, the present invention is explained in more detail with reference to Examples, but the present invention is not limited only to these Examples. The terms "part" and "%" are based on mass unless otherwise specified.

< Example 1 >

[0043] 250 parts of silver nitrate (Kishida Chemical Co., Ltd.) as a silver compound, 111 parts of glycine (Kanto Chemical Co., Inc.) as an amino acid (1 mol with respect to 1 mol of a silver ion), and 50 parts of 60% nitric acid (Kishida Chemical Co., Ltd.) as a pH adjuster were added to 9,589 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a silver compound aqueous solution (1).

[0044] 150 parts of hydrazine monohydrate (Kanto Chemical Co., Inc.) as a reducing agent, and 5 parts of 10% oleic acid methanol solution in which oleic acid (Kanto Chemical Co., Inc.) was dissolved in methanol as a dispersing agent were added to 845 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a reducing agent aqueous solution (1).

[0045] Using the forced thin film reactor ULREA (M-Technique Co., Ltd.), the silver compound aqueous solution (1) as the first fluid was sent at 500 mL/min, and the reducing agent aqueous solution (1) as the second fluid was sent at 50 mL/min. The solutions were introduced between the disks rotating at 500 rpm and mixed, and the discharged liquid was recovered from between the disks to obtain a slurry containing silver fine particles. In the example, the meanings of the first fluid and the second fluid are the same as those described in the forementioned JP 2010-189661.

[0046] Under the above condition, the forced thin film reactor ULREA was continuously operated for 30 minutes to produce silver fine particles. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the processing surfaces of the used discs were checked, and no silver adhesion was observed.

[0047] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders for each divided operation time were observed at a magnification of 10,000 times with a scanning electron microscope (JSM-7500F, JEOL Ltd.). An average value of the particle diameters of the 50 observed silver fine particles was calculated, and the average particle diameter was about 0.7 μm. It was confirmed that no difference of the particle diameter and shape from the start to the end of the operation of the forced thin film reactor was observed.

< Example 2 >

[0048] 250 parts of silver nitrate (Kishida Chemical Co., Ltd.) as a silver compound, 52 parts of L-arginine (Fujifilm Wako Pure Chemical Corporation) as an amino acid (0.2 mol with respect to 1 mol of a silver ion), and 5 parts of 60%

nitric acid (Kishida Chemical Co., Ltd.) as a pH adjuster were added to 9,693 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a silver compound aqueous solution (2).

[0049] 100 parts of hydrazine monohydrate (Kanto Chemical Co., Inc.) as a reducing agent, and 5 parts of 10% oleic acid methanol solution in which oleic acid (Kanto Chemical Co., Inc.) was dissolved in methanol as a dispersing agent were added to 895 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a reducing agent aqueous solution (2).

[0050] Using the forced thin film reactor ULREA (M-Technique Co., Ltd.), the silver compound aqueous solution (2) as the first fluid was sent at 500 mL/min, and the reducing agent aqueous solution (2) as the second fluid was sent at 50 mL/min. The solutions were introduced between the disks rotating at 500 rpm and mixed, and the discharged liquid was recovered from between the disks to obtain a slurry containing silver fine particles.

[0051] Under the above condition, the forced thin film reactor ULREA was continuously operated for 30 minutes to produce silver fine particles. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the processing surfaces of the used discs were checked, and no silver adhesion was observed.

[0052] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1, and the average particle diameter was about 0.6 μm. It was confirmed that no difference of the particle diameter and shape from the start to the end of the operation of the forced thin film reactor was observed.

< Example 3 >

[0053] 250 parts of silver nitrate (Kishida Chemical Co., Ltd.) as a silver compound, 243 parts of L-phenylalanine (Fujifilm Wako Pure Chemical Corporation) as an amino acid (1 mol with respect to 1 mol of a silver ion), and 5 parts of 60% nitric acid (Kishida Chemical Co., Ltd.) as a pH adjuster were added to 9,502 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a silver compound aqueous solution (3).

[0054] 225 parts of hydrazine monohydrate (Kanto Chemical Co., Inc.) as a reducing agent, and 5 parts of 10% oleic acid methanol solution in which oleic acid (Kanto Chemical Co., Inc.) was dissolved in methanol as a dispersing agent were added to 770 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a reducing agent aqueous solution (3).

[0055] Using the forced thin film reactor ULREA (M-Technique Co., Ltd.), the silver compound aqueous solution (3) as the first fluid was sent at 500 mL/min, and the reducing agent aqueous solution (3) as the second fluid was sent at 50 mL/min. The solutions were introduced between the disks rotating at 500 rpm and mixed, and the discharged liquid was recovered from between the disks to obtain a slurry containing silver fine particles.

[0056] Under the above condition, the forced thin film reactor ULREA was continuously operated for 30 minutes to produce silver fine particles. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the processing surfaces of the used discs were checked, and no silver adhesion was observed.

[0057] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1, and the average particle diameter was about 1.2 μm. It was confirmed that no difference of the particle diameter and shape from the start to the end of the operation of the forced thin film reactor was observed.

< Example 4 >

[0058] 250 parts of silver nitrate (Kishida Chemical Co., Ltd.) as a silver compound, 65 parts of L-glutamic acid (Fujifilm Wako Pure Chemical Corporation) as an amino acid (0.3 mol with respect to 1 mol of a silver ion), and 5 parts of 60% nitric acid (Kishida Chemical Co., Ltd.) as a pH adjuster were added to 9,680 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a silver compound aqueous solution (4). The same reducing agent aqueous solution as in Example 1 was prepared and used.

[0059] Using the forced thin film reactor ULREA (M-Technique Co., Ltd.), the silver compound aqueous solution (4) as the first fluid was sent at 500 mL/min, and the reducing agent aqueous solution (1) as the second fluid was sent at 50 mL/min. The solutions were introduced between the disks rotating at 500 rpm and mixed, and the discharged liquid was recovered from between the disks to obtain a slurry containing silver fine particles.

[0060] Under the above condition, the forced thin film reactor ULREA was continuously operated for 30 minutes to produce silver fine particles. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the processing surfaces of the used discs were checked, and no silver adhesion was observed.

[0061] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1, and the average particle diameter was about 0.9 μm. It was confirmed that no difference of the particle diameter and shape from the start to the end of the operation of the forced thin film reactor was observed.

< Comparative Example 1 >

[0062] 250 parts of silver nitrate (Kishida Chemical Co., Ltd.) as a silver compound, and 50 parts of 60% nitric acid (Kishida Chemical Co., Ltd.) as a pH adjuster were added to 9,700 parts of ion-exchanged water, and dissolved at 25°C under an air atmosphere to prepare a silver compound aqueous solution (5). The same reducing agent aqueous solution as in Example 1 was prepared and used.

[0063] Using the forced thin film reactor ULREA (M-Technique Co., Ltd.), the silver compound aqueous solution (5) as the first fluid was sent at 500 mL/min, and the reducing agent aqueous solution (1) as the second fluid was sent at 50 mL/min. The solutions were introduced between the disks rotating at 500 rpm and mixed, and the discharged liquid was recovered from between the disks to obtain a slurry containing silver fine particles.

[0064] Under the above condition, the forced thin film reactor ULREA was continuously operated for 3 minutes to produce silver fine particles. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. The processing surfaces of the used discs were checked, and silver adhesion was observed.

[0065] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1. It was confirmed that coarse particles of 10 μm or more, fine particles of 0.1 μm or less, and particles having an irregular shape gradually increased as time passed from the start of operation, and that the adhesion (necking) between particles became intense, and the particle diameter and shape significantly changed from the start of operation to the end of operation.

< Example 5 >

[0066] The silver compound aqueous solution (1) and the reducing agent aqueous solution (1) were prepared in the same manner as in Example 1, and used.

[0067] Silver fine particles were produced using a coaxial double pipe passage wherein an outer pipe passage has an inner diameter of 8 mm and an outer diameter of 10 mm, and an inner pipe passage has an inner diameter of 3 mm and an outer diameter of 4 mm. The silver compound aqueous solution (1) as the first fluid was sent at 500 mL/min to the outer pipe passage of the coaxial double pipe passage, and the reducing agent aqueous solution (1) as the second fluid was sent at 50 mL/min to the inner pipe passage of the coaxial double pipe passage. The solutions were contacted and mixed at the merging portion where the coaxial double pipe passage merges to form a single pipe passage, and the discharged liquid was recovered from between the single pipe passage to obtain a slurry containing silver fine particles.

[0068] Under the above condition, silver fine particles were continuously produced for 30 minutes. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the merging portion of the coaxial double pipe passage and the single pipe passage of the downstream thereof after use were confirmed, and no silver adhesion was observed.

[0069] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1, and the average particle diameter was about 0.9 μm. It was confirmed that no difference of the particle diameter and shape from the start to the end of the operation of the forced thin film reactor was observed.

< Comparative Example 2 >

[0070] The silver compound aqueous solution (5) and the reducing agent aqueous solution (1) were prepared in the same manner as in Comparative Example 1, and used.

[0071] Silver fine particles were produced using a coaxial double pipe passage wherein an outer pipe passage has an inner diameter of 8 mm and an outer diameter of 10 mm, and an inner pipe passage has an inner diameter of 3 mm and an outer diameter of 4 mm. The silver compound aqueous solution (5) as the first fluid was sent at 500 mL/min to the outer pipe passage of the coaxial double pipe passage, and the reducing agent aqueous solution (1) as the second fluid was sent at 50 mL/min to the inner pipe passage of the coaxial double pipe passage. The solutions were contacted and mixed at the merging portion where the coaxial double pipe passage merges to form a single pipe passage, and the discharged liquid was recovered from between the single pipe passage to obtain a slurry containing silver fine particles.

[0072] Under the above condition, silver fine particles were continuously produced for 10 minutes. In order to evaluate the silver fine particles, the discharged liquid was divided and collected every 1 minute of operation time. After the operation was completed, the merging portion of the coaxial double pipe passage and the single pipe passage of the downstream thereof of after use were confirmed, and silver adhesion was observed.

[0073] The silver fine particles contained in the slurry were filtered under reduced pressure using a hard filter paper (opening 1 μm), and the residue after filtration was washed with ion-exchanged water three times, dried, and then crushed to obtain silver powders. The obtained silver powders were observed with a scanning electron microscope in the same manner as in Example 1. It was confirmed that coarse particles of 10 μm or more, fine particles of 0.1 μm or less, and particles having an irregular shape gradually increased as time passed from the start of operation, and that the adhesion (necking) between particles became intense, and the particle diameter and shape significantly changed from the start of operation to the end of operation.

[0074] Table 1 summarizes the added amino acids, the production apparatus, the operation time, the presence or absence of adhesion, and the time-dependent change of the particle diameter and shape of the silver fine particles of Examples 1 to 5 and Comparative Examples 1 and 2.

[Table 1]

	Amino acid	Production apparatus	Operation time (min)	Presence of adhesion	Time-dependent change of particle diameter and shape
Example 1	Glycine	Forced thin film reactor	30	No	No
Example 2	L-Arginine	Forced thin film reactor	30	No	No
Example 3	L-Phenylalanine	Forced thin film reactor	30	No	No
Example 4	L-Glutamic acid	Forced thin film reactor	30	No	No
Example 5	Glycine	Coaxial double pipe passage	30	No	No
Comparative Example 1	-	Forced thin film reactor	3	Yes	Yes
Comparative Example 2	-	Coaxial double pipe passage	10	Yes	Yes

[0075] As can be seen from Table 1, in Comparative Examples 1 and 2 in which no amino acids were added, adhesion of silver was observed on the processing surface of the discs of the forced thin film reactor and the merging portion of the coaxial double pipe passage and the single pipe passage of the downstream thereof. On the other hand, in Examples 1 to 5 in which amino acids were added, no adhesion of silver was observed. The time-dependent changes of the particle diameter and shape of the silver fine particles observed in Comparative Examples 1 and 2 were not observed in Examples 1 to 5.

[0076] As described above, in the method of producing silver fine particles of the present invention, silver does not adhere to the inner walls of the merging portion and the flow path of the continuous reactor. As a result, the shape and properties of the silver fine particles to be produced can be controlled without changing the environment of the merging portion and the flow path with lapse of time, and silver fine particles having a certain quality can be produced. Therefore, according to the method of producing silver fine particles of the present invention, silver fine particles can be produced in a wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, without using a large amount of ammonia causing deterioration of working environment.

INDUSTRIAL APPLICABILITY

[0077] The present invention provides a method of producing silver fine particles in the wet reduction method using a continuous reactor with sufficient continuous productivity and quality uniformity, without problems of deterioration of working environment and generation of explosive fulminating silver due to the use of a large amount of ammonia.

Claims

1. A method of producing silver fine particles, comprising continuously reducing silver ions contained in a silver compound to precipitate silver fine particles by introducing at least two fluids from separate flow paths and mixing the fluids,

   wherein one fluid of the at least two fluids contains the silver compound, and another fluid contains a reducing agent, and
   at least one fluid of the at least two fluids contains an amino acid.

2. The method of producing silver fine particles according to claim 1, wherein formation of a silver mirror is suppressed by the amino acid.

3. The method of producing silver fine particles according to claim 1 or 2, wherein the amino acid is contained in the fluid containing the silver compound.

4. The method of producing silver fine particles according to any one of claims 1 to 3, wherein 0.1 to 4 mol of the amino acid is used with respect to 1 mol of the silver ion.

5. The method of producing silver fine particles according to any one of claims 1 to 4, wherein a concentration of the silver ion in the fluid containing the silver compound is 0.1 to 5% by mass.

6. The method of producing silver fine particles according to any one of claims 1 to 5, wherein a dispersing agent is contained in at least one fluid of the at least two fluids.

7. The method of producing silver fine particles according to any one of claims 1 to 6, wherein the amino acid is glycine.

8. The method of producing silver fine particles according to any one of claims 1 to 7, wherein the at least two fluids are mixed between at least two processing surfaces arranged so as to be capable of approaching to and separating from each other, at least one of which rotates relative to the other.

9. The method of producing silver fine particles according to any one of claims 1 to 8, wherein ammonia is not used.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
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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. B22F9/00-9/30, B22F1/00

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	1971-2020
Registered utility model specifications of Japan	1996-2020
Published registered utility model applications of Japan	1994-2020

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	JP 2005-254179 A (BANDO CHEMICAL INDUSTRIES, LTD.) 22 September 2005, paragraphs [0016]-[0026]	1-2, 4-7, 9
X Y	JP 2009-533558 A (BAYER TECHNOLOGY SERVICES GMBH) 17 September 2009, claims, paragraphs [0032]-[0038], [0046]-[0049], [0071], [0072], fig. 2	1-7, 9 8-9
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A	JP 2018-197392 A (SHINKO KAGAKU KOGYOSHO KK) 13 December 2018, claims, paragraphs [0092]-[0098]	1-9

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

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INTERNATIONAL SEARCH REPORT

International application No.	PCT/JP2019/046681

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2019/046681

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