(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 357 488 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
24.04.2024 Bulletin 2024/17

(21) Application number: **22824733.4**

(22) Date of filing: **18.05.2022**

(51) International Patent Classification (IPC):
C25D 15/02 $^{(2006.01)}$ ***C25D 21/14*** $^{(2006.01)}$
C25D 21/18 $^{(2006.01)}$

(52) Cooperative Patent Classification (CPC):
C23C 18/52; C25D 3/12; C25D 15/00; C25D 15/02;
C25D 21/14; C25D 21/18

(86) International application number:
PCT/JP2022/020620

(87) International publication number:
WO 2022/264739 (22.12.2022 Gazette 2022/51)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **16.06.2021 JP 2021100239**

(71) Applicant: **JCU Corporation**
Tokyo 1100015 (JP)

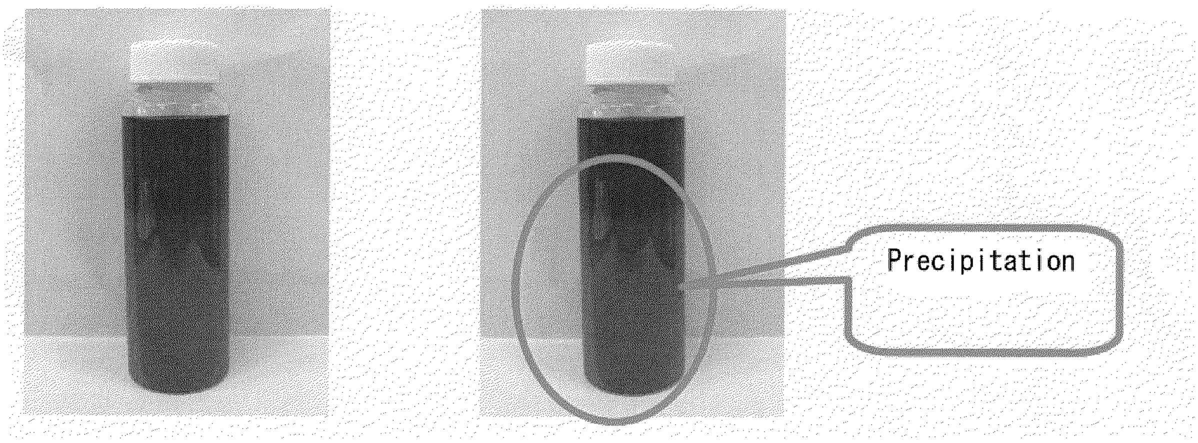
(72) Inventors:
- **SHIBATA, Kana**
  Kawasaki-shi, Kanagawa 215-0033 (JP)
- **NISHIKAWA, Kenichi**
  Kawasaki-shi, Kanagawa 215-0033 (JP)

(74) Representative: **Wächtershäuser & Hartz**
Patentanwaltspartnerschaft mbB
Weinstraße 8
80333 München (DE)

(54) ADDITIVE FOR COMPOSITE PLATING SOLUTIONS

(57) An additive for a composite plating solution characterized by containing non-conductive fine particles, nickel ions, and water is a liquid containing the non-conductive fine particles, does not require preparation of special fine particles, and has high stability.

[FIG. 2]



EP 4 357 488 A1

Description

Technical Field

[0001] The present invention relates to a technique for causing an additive containing non-conductive fine particles used in a composite plating solution to become a liquid.

Background Art

[0002] Plating that has a non-shiny uniform semi-bright or almost matte appearance is called satin nickel. A method for obtaining a satin-like appearance includes composite plating in which non-conductive fine particles are suspended in a liquid and codeposited with nickel (NPL 1).

[0003] In addition, plating utilizing similar non-conductive fine particles includes microporous plating used for a base for chrome plating used as decorative plating for an automobile part, a faucet fitting, or the like. With this microporous plating film, a large number of invisible tiny pores can be formed in the surface layer of chrome plating, and corrosion resistance can be improved by dispersing a corrosion current (PTL 1). This microporous plating is also a type of composite plating.

[0004] The fine particles used to form a satin-like appearance or micropores have a very small particle diameter, and therefore scatter into the atmosphere when added to the plating solution, are exposed to a worker or adhere to the surroundings in working, and a liquid additive form has long been desired.

[0005] However, as for an additive in which water is used as a solvent, when non-conductive fine particles such as silica particles were added thereto, a phenomenon in which the non-conductive fine particles sediment, precipitate, and then solidify after several hours was observed, and it was unsuitable as a stable fine particle liquid additive.

[0006] Incidentally, as a technique for forming micropores during plating, it is known to perform electroplating using a plating solution containing non-conductive particles such as silica particles that are positively charged using aluminum hydroxide (PTL 2) .

[0007] However, if positively charged non-conductive fine particles are prepared in advance as an additive by such a conventional technique, the particles will solidify, so that it is necessary to add the particles separately each time when used, which made it unsuitable as a stable fine particle liquid additive.

Citation List

Patent Literature

[0008]

PTL 1: JPH03-291395A
PTL 2: JPH04-371597A

Non Patent Literature

[0009] NPL 1: Electroplating & Chemical Plating Guide Book, 1987 Edition, Tokyo Plating Material Cooperative Association, P. 151

Summary of Invention

Technical Problem

[0010] Therefore, an object of the invention is to provide an additive for a composite plating solution, which is a liquid containing non-conductive fine particles, does not require preparation of special fine particles, and has high stability.

Solution to Problem

[0011] The present inventors conducted intensive studies to solve the above problems, and as a result, they found that the above problems can be solved by incorporating nickel ions for dispersing non-conductive fine particles in a liquid, and thus completed the invention.

[0012] That is, the invention is directed to an additive for a composite plating solution characterized by containing non-conductive fine particles, nickel ions, and water.

[0013] In addition, the invention is directed to a method for preventing solidification of a precipitate of non-conductive fine particles in an additive for a composite plating solution, characterized by incorporating nickel ions in an additive for a composite plating solution containing non-conductive fine particles and water.

Advantageous Effects of Invention

[0014] The additive for a composite plating solution of the invention can prevent sedimentation of non-conductive fine particles (separation between a suspension layer of non-conductive fine particles and a supernatant is delayed: a time until formation of a precipitate is slow), and prevent solidification of a precipitate (non-conductive fine particles do not re-disperse even if shaking is performed), and can maintain a stable state as a liquid additive.

[0015] Therefore, the additive for a composite plating solution of the invention can be used stably without scattering into the atmosphere when added to the plating solution, or exposure to a worker or adhesion to the surroundings in working.

Brief Description of Drawings

[0016]

[FIG. 1] FIG. 1 is a view showing a state of an additive of Comparative Example 1 after being left for 168 hours in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 2] FIG. 2 is a view showing a state of an additive of Example 1 after being left for 168 hours in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 3] FIG. 3 is a view showing a state of an additive of Example 2 after being left for 168 hours in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 4] FIG. 4 is a view showing a state of an additive of Comparative Example 1 after being left for 168 hours and then being shaken in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 5] FIG. 5 is a view showing a state of an additive of Example 1 after being left for 168 hours and then being shaken in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 6] FIG. 6 is a view showing a state of an additive of Example 2 after being left for 168 hours and then being shaken in Test Example 2 (the left and right views are the same, and the right view has an explanation added to the left view).

[FIG. 7] FIG. 7 is a view showing an appearance of a test piece used in Test Example 3.

Description of Embodiments

[0017] The additive for a composite plating solution of the invention (hereinafter referred to as "the additive of the invention") contains non-conductive fine particles, nickel ions, and water.

[0018] The non-conductive fine particles used in the additive of the invention are not particularly limited, and examples thereof include oxides, nitrides, sulfides, and inorganic salts of metals such as silicon, barium, zirconium, aluminum and titanium. Among these, oxides, nitrides, sulfides, and inorganic salts of silicon, barium, zirconium, and aluminum are preferred in terms of effect, and oxides such as silica (silicon dioxide) and zirconia (zirconium dioxide), and inorganic salts such as barium sulfate are particularly preferred. Among these non-conductive fine particles, one type or two or more types can be used.

[0019] In addition, as the non-conductive fine particles, for example, commercially available products such as MP POWDER 308 and MP POWDER 309A of JCU CORPORATION can also be used.

[0020] The average particle diameter of these non-conductive fine particles is not particularly limited, but is, for example, 0.1 to 10 um, and preferably 1.0 to 3.0 um. The average particle diameter is a value measured by a zeta potential/particle diameter/molecular weight measurement system ELSZ-2000 manufactured by Otsuka Electronics Co., Ltd.

[0021] The content of the non-conductive fine particles in the additive of the invention is not particularly limited, but is, for example, 0.01 to 20 wt% (hereinafter simply referred to as "%"), and preferably 0.05 to 10%. In addition, the content of the non-conductive fine particles in the additive of the invention can also be set to a concentration higher than when the non-conductive fine particles are used in an ordinary composite plating solution. In this case, the content is, for example, 5 to 50%, and preferably 10 to 40%.

[0022] The content of nickel ions in the additive of the invention is not particularly limited, but is, for example, 0.01 to 12%, and preferably 0.05 to 10%.

[0023] The nickel ion supply source of the nickel ions is not particularly limited as long as nickel ions are generated when it is dissolved in water. Examples thereof include nickel sulfate, nickel chloride, nickel sulfamate, and nickel acetate.

These can be used in the form of a hydrate or an anhydride. Among these, nickel sulfate hexahydrate is preferred in terms of cost and containing no halogens. Among these nickel ion supply sources, one type or two or more types can be used.

[0024] The mass ratio of the non-conductive fine particles and the nickel ions in the additive of the invention may be appropriately set according to the type of non-conductive fine particles, but for example, when silicon dioxide is used as the non-conductive fine particles, the mass ratio is 1:0.001 to 1:3, and preferably 1:0.003 to 1:2.

[0025] The water used in the additive of the invention is not particularly limited, and for example, distilled water, ion-exchanged water, ultrapure water, city water, or the like may be used.

[0026] The pH of the additive of the invention is not particularly limited, but is preferably neutral or acidic, and in particular, since a hydroxide of nickel is generated at pH 6 or higher, it is more preferably pH 6 or lower. In order to adjust the pH, for example, an inorganic acid such as sulfuric acid, hydrochloric acid, or nitric acid, an organic acid such as acetic acid, sulfamic acid, or the like may be used.

[0027] The additive of the invention can prevent sedimentation of the non-conductive fine particles and solidification of a precipitate thereof in the additive for composite plating solution containing water and the non-conductive fine particles by the action of nickel ions described above, and can maintain a stable state as a liquid additive, but may further contain one type or two or more types selected from a charge imparting agent, a surfactant, and a brightener.

[0028] Examples of the charge imparting agent include aluminum ions. The supply source of the aluminum ions is not particularly limited, but when it is added to a composite plating solution containing a Watts bath in which nickel sulfate or nickel chloride is used as a base, use of polyaluminum chloride or aluminum sulfate has little effect on sulfate ions or chlorine ions.

[0029] When polyaluminum chloride is incorporated in the additive of the invention, polyaluminum chloride in the form of a powder may be added, or for example, a commercially available product in the form of an aqueous solution of about 10% in terms of aluminum oxide such as PAC of Nankai Chemical Industry Co., Ltd. or TAIPAC series of Taimei Chemicals Co., Ltd. may be added. Such polyaluminum chloride may be added as it is or after being appropriately diluted or the like.

[0030] The content of polyaluminum chloride in the additive of the invention is not particularly limited, but is, for example, 0.01 to 50.0%, and preferably 0.1 to 30% in terms of aluminum oxide (for example, 0.002 to 15%, and preferably 0.02 to 7% in terms of aluminum).

[0031] Further, when aluminum sulfate is incorporated in the additive of the invention, aluminum sulfate in the form of a powder may be added, or aluminum sulfate in the form of a liquid may be added. To aluminum sulfate in the form of a liquid, a commercially available product such as an aluminum sulfate solution for tap water or an aluminum sulfate solution for general use of Taimei Chemical Co., Ltd. may be added.

[0032] The surfactant is not particularly limited, but examples thereof include nonionic surfactants such as polyethylene glycol, anionic surfactants such as sodium polyoxyethylene alkyl ether sulfates, cationic surfactants such as benzethonium chloride, stearylamine acetate, and dodecyltrimethylammonium chloride, and amphoteric surfactants such as lauryl betaine, lauryl dimethylamino acetate betaine, amidopropyl dimethylamino acetate betaine laurate, and lauryl dimethylamine oxide. Among these surfactants, one type or two or more types can be used. Among these surfactants, a cationic surfactant that is positively charged or an amphoteric surfactant that exhibits cationic in a pH range where it is used is preferred. With the use of such a surfactant, the dispersibility is further maintained.

[0033] The content of the surfactant in the additive of the invention is not particularly limited, but is, for example, 0.001 to 5%, and preferably 0.001 to 2%.

[0034] The brightener is not particularly limited, and examples thereof include a primary brightener and a secondary brightener that are used in an ordinary composite plating solution. Examples of the primary brightener include sulfonamides, sulfonimides, benzenesulfonic acid, and alkylsulfonic acids. As the primary brightener, for example, MP333 (manufactured by JCU CORPORATION) or the like is commercially available and therefore may be used. Examples of the secondary brightener include 1,4-butynediol and coumarin. The secondary brightener is an organic compound having a functional group as follows (C=O, C=C, C=C, C=N, C=N, N-C=S, N=N, $-CH_2-CH-O$). As the secondary brightener, for example, #810 (manufactured by JCU CORPORATION) is commercially available and therefore may be used. These primary brighteners and secondary brighteners may be used alone or a plurality thereof may be used in combination.

[0035] The content of the brightener in the additive of the invention is not particularly limited, but for example, the primary brightener is preferably added in an amount of 0.1 to 900 mL/L, and the secondary brightener is preferably added in an amount of about 0.1 to 900 mL/L.

[0036] It is only necessary that the additive of the invention contains non-conductive fine particles, nickel ions, and water, and therefore, an electrolytic nickel solution that is used for a composite plating solution such as a Watts bath or a sulfamate bath may be utilized as one containing nickel ions and water.

[0037] The composition of the Watts bath includes the following composition. This Watts bath may be diluted as appropriate.

Nickel sulfate ($NiSO_4 \cdot 6H_2O$): 1 to 450 g/L

Nickel chloride ($NiCl_2 \cdot 6H_2O$): 0.1 to 45 g/L
Boric acid (H_3BO_3) : 0.1 to 45 g/L
Water: balance

[0038] When the Watts bath is utilized in this manner, the additive of the invention becomes one containing non-conductive fine particles and the Watts bath.

[0039] The composition of the sulfamate bath includes the following composition. This sulfamate bath may be diluted as appropriate.

Nickel sulfamate ($Ni(SO_3NH_2)_2 \cdot 4H_2O$): 1 to 600 g/L
Nickel chloride ($NiCl_2 \cdot 6H_2O$): 0 to 15 g/L
Boric acid (H_3BO_3) : 0.1 to 40 g/L
Water: balance

[0040] When the sulfamate bath is utilized in this manner, the additive of the invention becomes one containing non-conductive fine particles and the sulfamate bath.

[0041] Examples of the additive of the invention include those containing non-conductive fine particles, nickel ions, and water as described above, but the following ones may also be used.

(1) An additive for a composite plating solution characterized by containing non-conductive fine particles, nickel ions, and water.
(2) The additive for a composite plating solution according to (1), wherein the composite plating solution is a satin nickel plating solution or a microporous nickel plating solution.
(3) The additive for a composite plating solution according to (1) or (2), wherein the non-conductive fine particles are one or more types selected from oxides, nitrides, sulfides, and inorganic salts of silicon, barium, zirconium, aluminum, and titanium.
(4) The additive for a composite plating solution according to any one of (1) to (3), wherein the supply source of nickel ions is one type or two or more types selected from nickel sulfate hexahydrate, nickel chloride, and nickel sulfamate.
(5) An additive for a composite plating solution characterized by containing:

non-conductive fine particles;
nickel ions; and
one or more types selected from a charge imparting agent, a surfactant, and a brightener.

(6) An additive for a composite plating solution characterized by containing:

non-conductive fine particles; and
a Watts bath or a sulfamate bath.

(7) An additive for a composite plating solution characterized by containing:

non-conductive fine particles;
a Watts bath or a sulfamate bath; and
one or more types selected from a charge imparting agent, a surfactant, and a brightener.

(8) A method for preventing solidification of a precipitate of non-conductive fine particles in an additive for a composite plating solution, characterized by incorporating nickel ions in an additive for a composite plating solution containing non-conductive fine particles and water.

[0042] The additive of the invention described above can be prepared by stirring and mixing the above-mentioned components until homogeneity.

[0043] Then, it is possible to prevent sedimentation of the non-conductive fine particles of the invention or solidification of a precipitate thereof, and maintain a stable state as a liquid additive.

[0044] It is possible to prepare a composite plating solution such as a satin nickel plating solution or a microporous nickel plating solution by adding the additive of the invention to a composite plating solution base. In particular, by adding the additive of the invention to a microporous nickel plating solution base to prepare a microporous nickel plating solution, it is possible to perform microporous plating with a good number of micropores as in a conventional case. The composite plating solution base refers to a base containing some or all of the components other than the non-conductive fine particles in the composite plating solution, and becoming the composite plating solution by adding the additive of the invention thereto.

Examples

[0045] Hereinafter, the invention will be described in detail with reference to Examples, but the invention is by no means limited to these Examples or the like. In the preparation of additives in Examples and Comparative Examples, a 110 mL glass screw tube bottle (9-852-10, manufactured by AS ONE Co., Ltd.) (hereinafter referred to as a screw tube bottle) was used.

Example 1

Preparation of Additive Using Nickel Salt:

[0046] In a screw tube bottle, 100 mL of a 500 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 5.31).

Example 2

Preparation of Additive Using Watts Bath:

[0047] In a screw tube bottle, 100 mL of a Watts bath prepared with the following composition and 6 g of a powder of silicon dioxide (average particle diameter: 1.5 um) were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.69).

<Watts Bath>

[0048]

Nickel sulfate ($NiSO_4 \cdot 6H_2O$): 250 g/L
Nickel chloride ($NiCl_2 \cdot 6H_2O$): 40 g/L
Boric acid (H_3BO_3) : 40 g/L

Example 3

Preparation of Additive Using Nickel Salt:

[0049] In a screw tube bottle, 100 mL of a 500 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further polyaluminum chloride (PAC, Nankai Chemical Co., Ltd.) in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.92).

Example 4

Preparation of Additive Using Nickel Salt:

[0050] In a screw tube bottle, 100 mL of a 60 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.99).

Example 5

Preparation of Additive Using Nickel Salt:

[0051] In a screw tube bottle, 100 mL of a 10 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 4.05).

Example 6

Preparation of Additive Using Nickel Salt:

[0052] In a screw tube bottle, 100 mL of a 1 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.86).

Example 7

Preparation of Additive Using Nickel Salt:

[0053] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 450 g/L of nickel sulfate, 40 g/L of nickel chloride, and 40 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.62).

Example 8

Preparation of Additive Using Nickel Salt:

[0054] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 250 g/L of nickel sulfate, 40 g/L of nickel chloride, and 40 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.74).

Example 9

Preparation of Additive Using Nickel Salt:

[0055] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 10 g/L of nickel sulfate, 1.6 g/L of nickel chloride, and 1.6 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.96).

Example 10

Preparation of Additive Using Nickel Salt:

[0056] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 1 g/L of nickel sulfate, 0.16 g/L of nickel chloride, and 0.16 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further polyaluminum chloride in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.85) .

Example 11

Preparation of Additive Using Nickel Salt:

[0057] In a screw tube bottle, 100 mL of a 500 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.31).

Example 12

Preparation of Additive Using Nickel Salt:

[0058] In a screw tube bottle, 100 mL of a 60 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.24).

Example 13

Preparation of Additive Using Nickel Salt:

[0059] In a screw tube bottle, 100 mL of a 10 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.41).

Example 14

Preparation of Additive Using Nickel Salt:

[0060] In a screw tube bottle, 100 mL of a 1 g/L aqueous solution of nickel sulfate and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.31).

Example 15

Preparation of Additive Using Nickel Salt:

[0061] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 450 g/L of nickel sulfate, 40 g/L of nickel chloride, and 40 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.08).

Example 16

Preparation of Additive Using Nickel Salt:

[0062] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 250 g/L of nickel sulfate, 40 g/L of nickel chloride, and 40 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.00).

Example 17

Preparation of Additive Using Nickel Salt:

[0063] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 10 g/L of nickel sulfate, 1.6 g/L of nickel chloride, and 1.6 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.30).

Example 18

Preparation of Additive Using Nickel Salt:

[0064] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 1 g/L of nickel sulfate, 0.16 g/L of nickel chloride, and 0.16 g/L of boric acid, and 6 g of a powder of silicon dioxide, and further aluminum sulfate in an amount of 0.07 g in terms of aluminum were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.30) .

Example 19

Preparation of Additive Using Nickel Salt:

[0065] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 100 g/L of nickel sulfate and 6 g of a powder of silicon dioxide were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 5.63).

Example 20

Preparation of Additive Using Nickel Salt:

[0066] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 100 g/L of nickel sulfate and 6 g of a powder of titanium dioxide (average particle diameter: 0.01 um) were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 4.94).

Example 21

Preparation of Additive Using Nickel Salt:

[0067] In a screw tube bottle, 100 mL of an aqueous solution adjusted to 100 g/L of nickel sulfate and 6 g of a powder of zirconium silicate (average particle diameter: 1.1 um) were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 5.64).

[0068] As Comparative Examples, cases where nickel ions were not contained in the dispersion solvent for the non-conductive fine particles, and water was substantially used as the main solvent will be described below.

Comparative Example 1

Preparation of Additive Prepared with Only Water:

[0069] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of silicon dioxide were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 7.17) .

Comparative Example 2

Preparation of Additive Prepared with Only Water:

[0070] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of titanium dioxide were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 7.61) .

Comparative Example 3

Preparation of Additive Prepared with Only Water:

[0071] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of zirconium silicate were placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 6.91) .

Comparative Example 4

Preparation of Additive Prepared with Only Water:

[0072] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of silicon dioxide were placed, followed by stirring and mixing until homogeneity, and an additive adjusted to pH 3 or lower with a small amount of sulfuric acid was obtained (pH 2.34) .

Comparative Example 5

Preparation of Additive Prepared with Only Water:

[0073] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of silicon dioxide were placed, and further, polyaluminum chloride in an amount of 0.07 g in terms of aluminum was placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.36).

Comparative Example 6

Preparation of Additive with Only Water:

[0074] In a screw tube bottle, 100 mL of pure water and 6 g of a powder of silicon dioxide were placed, and further, aluminum sulfate in an amount of 0.07 g in terms of aluminum was placed, followed by stirring and mixing until homogeneity, thereby obtaining an additive (pH 3.84).

Test Example 1

Dispersibility Test:

[0075] The screw tube bottles were sealed in a state where the additives of Examples 1 to 21 and Comparative Examples 1 to 6 were placed therein, and shaking was performed until homogeneity, and then, the state of each additive was investigated after 24 hours passed. When precipitation occurred, shaking was performed again and redispersibility of the non-conductive fine particles was investigated. In the shaking, the screw tube bottle was shaken up and down 30 times. After shaking, it was visually evaluated whether precipitation occurred in the additive after 24 hours passed, and further redispersibility after shaking was performed again was evaluated according to the following criteria. The results are shown in Table 1.

<Redispersibility Evaluation Criteria>

Evaluation Contents

[0076]

A: Homogeneity is achieved when shaking is performed.
B: Homogeneity is not achieved even when shaking is performed.

[Table 1]

	Precipitation	Redispersibility		Precipitation	Redispersibility
Example 1	slightly occurred	A	Example 15	slightly occurred	A
Example 2	occurred	A	Example 16	occurred	A
Example 3	occurred	A	Example 17	occurred	A
Example 4	occurred	A	Example 18	occurred	A
Example 5	occurred	A	Example 19	occurred	A
Example 6	occurred	A	Example 20	occurred	A
Example 7	slightly occurred	A	Example 21	occurred	A
Example 8	slightly occurred	A			
Example 9	slightly occurred	A	Comparative Example 1	occurred	B

(continued)

	Precipitation	Redispersibility		Precipitation	Redispersibility
Example 10	slightly occurred	A	Comparative Example 2	occurred	A
Example 11	slightly occurred	A	Comparative Example 3	occurred	B
Example 12	occurred	A	Comparative Example 4	occurred	B
Example 13	occurred	A	Comparative Example 5	occurred	A
Example 14	occurred	A	Comparative Example 6	occurred	A

[0077] With respect to Examples 1 to 21, although precipitation occurred, when shaking was performed again, the precipitate easily redispersed, and homogeneous dispersibility could be verified.

[0078] On the other hand, with respect to Comparative Examples 1, 3, and 4, precipitation occurred, and even after shaking was performed again, the precipitate solidified and did not redisperse. Further, with respect to Comparative Examples 2, 5, and 6, although precipitation occurred, when shaking was performed again, the precipitate easily redispersed, and homogeneous dispersibility could be verified.

Test example 2

Dispersibility Test After Long-Term Storage:

[0079] The screw tube bottles were sealed in a state where the additives of Examples 1 to 21 and Comparative Examples 1 to 6 were placed therein, and shaking was performed until homogeneity, and then, the state of each additive was investigated after 168 hours passed. When precipitation occurred, shaking was performed again and redispersibility of the non-conductive fine particles was investigated. In the shaking, the screw tube bottle was shaken up and down 30 times. After shaking, it was visually evaluated whether precipitation occurred in the additive after 168 hours passed, and redispersibility after shaking was performed again was evaluated according to the same criteria as in Test Example 1. The results are shown in Table 2.

[0080] Further, the results of the additive of Comparative Example 1 are shown in FIGS. 1 and 4, the results of the additive of Example 1 are shown in FIGS. 2 and 5, and the results of the additive of Example 2 are shown in FIGS. 3 and 6.

[Table 2]

	Precipitation	Redispersibility		Precipitation	Redispersibility
Example 1	occurred	A	Example 15	occurred	A
Example 2	occurred	A	Example 16	occurred	A
Example 3	occurred	A	Example 17	occurred	A
Example 4	occurred	A	Example 18	occurred	A
Example 5	occurred	A	Example 19	occurred	A
Example 6	occurred	A	Example 20	occurred	A
Example 7	occurred	A	Example 21	occurred	A
Example 8	occurred	A			
Example 9	occurred	A	Comparative Example 1	occurred	B
Example 10	occurred	A	Comparative Example 2	occurred	A
Example 11	occurred	A	Comparative Example 3	occurred	B
Example 12	occurred	A	Comparative Example 4	occurred	B

(continued)

	Precipitation	Redispersibility		Precipitation	Redispersibility
Example 13	occurred	A	Comparative Example 5	occurred	A
Example 14	occurred	A	Comparative Example 6	occurred	B

[0081] With respect to Examples 1 to 21, although precipitation occurred, when shaking was performed again, the precipitate easily redispersed, and homogeneous dispersibility could be verified.

[0082] On the other hand, with respect to Comparative Examples 1, 3, 4, and 5, precipitation occurred, and even after shaking was performed again, the precipitate solidified and did not redisperse. Further, with respect to Comparative Examples 2 and 5, although precipitation occurred, when shaking was performed again, the precipitate easily redispersed, and homogeneous dispersibility could be verified.

[0083] From the results of Test Examples 1 and 2, it was found that in order to form a liquid state with good dispersibility without causing precipitation of the non-conductive fine particles and solidification of the precipitate thereof, incorporation of nickel ions together with the non-conductive fine particles has an effect on redispersibility.

Test Example 3

Plating Test:

[0084] The additive prepared in Example 1 was added in an amount of 0.5 mL/L to a plating bath having the following composition, thereby preparing a microporous plating solution.

<Plating Bath>

[0085]

Nickel sulfate ($NiSO_4 \cdot 6H_2O$): 260 g/L
Nickel chloride ($NiCl_2 \cdot 6H_2O$): 45 g/L
Boric acid (H_3BO_3) : 45 g/L
Brightener #810*: 3 mL/L
Brightener MP333*: 10 mL/L
Polyaluminum chloride: 0.3 mg/L (in terms of aluminum)
Bath temperature: 55°C
Specific gravity: 1.205
*: manufactured by JCU CORPORATION

[0086] Subsequently, a microporous plated product was produced as a test piece according to the following steps using a bent cathode test piece (brass: manufactured by Yamamoto-MS Co., Ltd.) having a shape shown in FIG. 7.

(Degreasing/Acid Activation)

[0087] The test piece was treated with SK-144 (manufactured by JCU CORPORATION) for 5 minutes for degreasing, and then treated with V-345 (manufactured by JCU CORPORATION) for 30 seconds for acid activation.

(Bright Nickel Plating)

[0088] The test piece subjected to the degreasing and acid activation treatments above were plated in the following nickel plating solution at 4 A/dm^2 for 3 minutes.

<Bright Nickel Plating Bath>

[0089]

Nickel sulfate ($NiSO_4 \cdot 6H_2O$): 260 g/L
Nickel chloride ($NiCl_2 \cdot 6H_2O$): 45 g/L

Boric acid (H_3BO_3) : 45 g/L
Brightener #810*: 3 mL/L
Brightener #83*: 10 mL/L
*: manufactured by JCU CORPORATION

(Microporous Plating)

[0090] The test piece subjected to bright plating was plated in the microporous plating solution prepared above at 3 A/dm^2 for 3 minutes.

(Chrome Plating)

[0091] The test piece subjected to microporous nickel plating above was plated in a hexavalent chromium plating solution having the following composition at 10 A/dm^2 for 3 minutes.

<Hexavalent Chromium Plating Bath>

[0092]

Chromic anhydride (CrO_3): 250 g/L
Sulfuric acid (H_2SO_4) : 1 g/L
Additive ECR 300LN*: 10 mL/L
MISTSHUT NP*: 0.1 mL/L
*: manufactured by JCU CORPORATION

(Procedure 1 for Measuring Number of Micropores)

[0093] The test piece after chrome plating was immersed in a copper sulfate plating solution having the following composition for 3 minutes, and then plated in the copper sulfate plating solution at 0.5 A/dm^2 for 3 minutes.

<Copper Sulfate Plating Bath>

[0094]

Copper sulfate ($CuSO_4 \cdot 5H_2O$): 220 g /L
Sulfuric acid (H_2SO_4): 50 g/L
Hydrochloric acid (HCl): 0.15 mL/L

(Procedure 2 for Measuring Number of Micropores)

[0095] After copper sulfate plating, the test piece was gently washed with water, air-dried, and then, the number of micropores in the plating film was measured. The measurement of the number of micropores was performed for the evaluation surface of the test piece using a microscope VHX-200 manufactured by KEYENCE CORPORATION. The measurement result of the number of micropores is shown in Table 3.

[Table 3]

Number of micropores in evaluation surface (micropores/cm^2)	30440

[0096] With the use of the additive of the invention, the expected number of micropores could be obtained even when a microporous nickel plating solution was prepared by adding non-conductive fine particles in a liquid state.

Industrial Applicability

[0097] The additive of the invention can be utilized for preparing a composite plating solution.

Claims

1. An additive for a composite plating solution, **characterized by** comprising non-conductive fine particles, nickel ions, and water.

2. The additive for a composite plating solution according to claim 1, wherein the composite plating solution is a satin nickel plating solution or a microporous nickel plating solution.

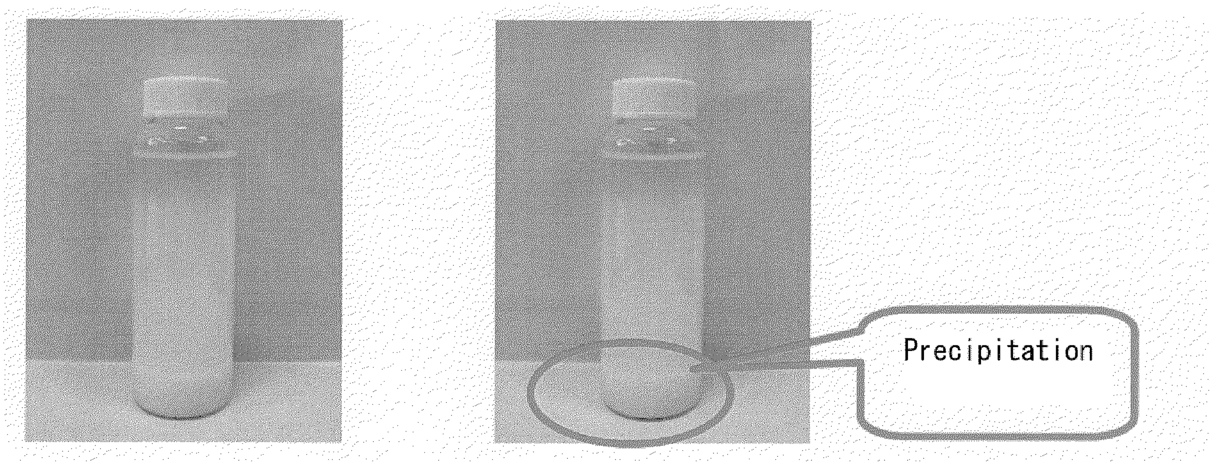
3. The additive for a composite plating solution according to claim 1 or 2, wherein the non-conductive fine particles are one type or two or more types of oxides, nitrides, sulfides, or inorganic salts of a metal selected from the group consisting of silicon, barium, zirconium, aluminum, and titanium.

4. The additive for a composite plating solution according to any one of claims 1 to 3, which contains one type or two or more types selected from the group consisting of hydrates of nickel sulfate, nickel chloride, nickel sulfamate, and nickel acetate and anhydrides of nickel sulfate, nickel chloride, nickel sulfamate, and nickel acetate.

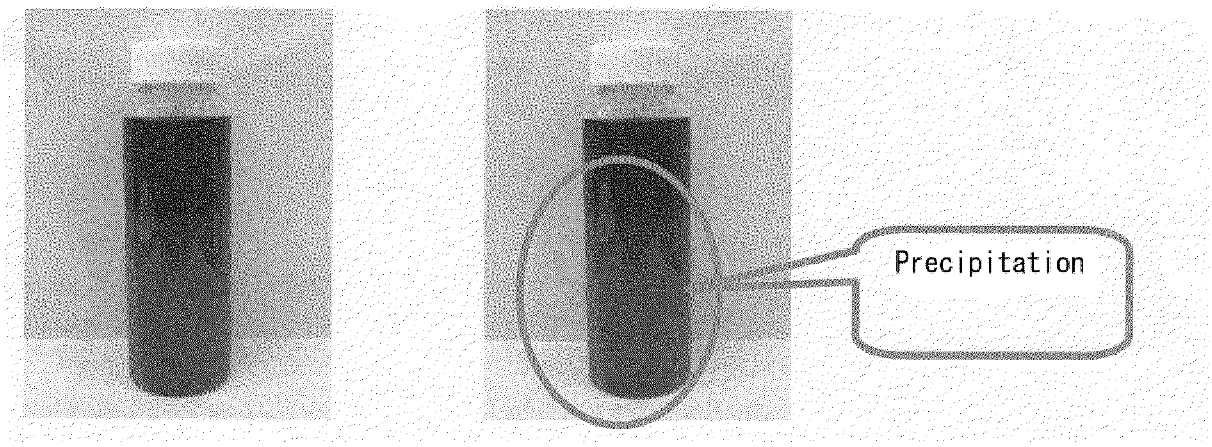
5. The additive for a composite plating solution according to any one of claims 1 to 4, further comprising one type or two or more types selected from a charge imparting agent, a surfactant, and a brightener.

6. A method for preventing solidification of a precipitate of non-conductive fine particles in an additive for a composite plating solution, **characterized by** incorporating nickel ions in an additive for a composite plating solution containing non-conductive fine particles and water.

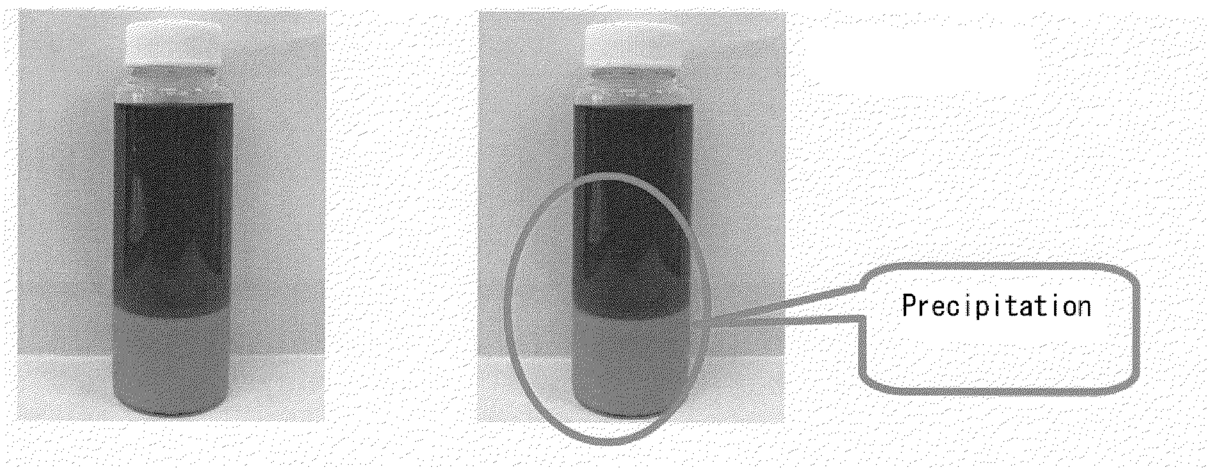
[FIG. 1]



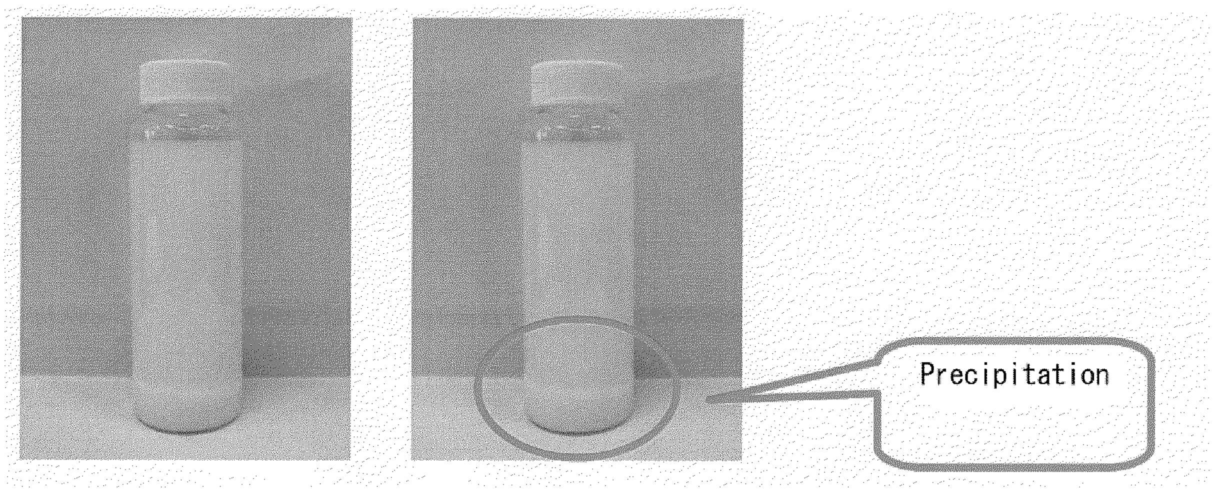
[FIG. 2]



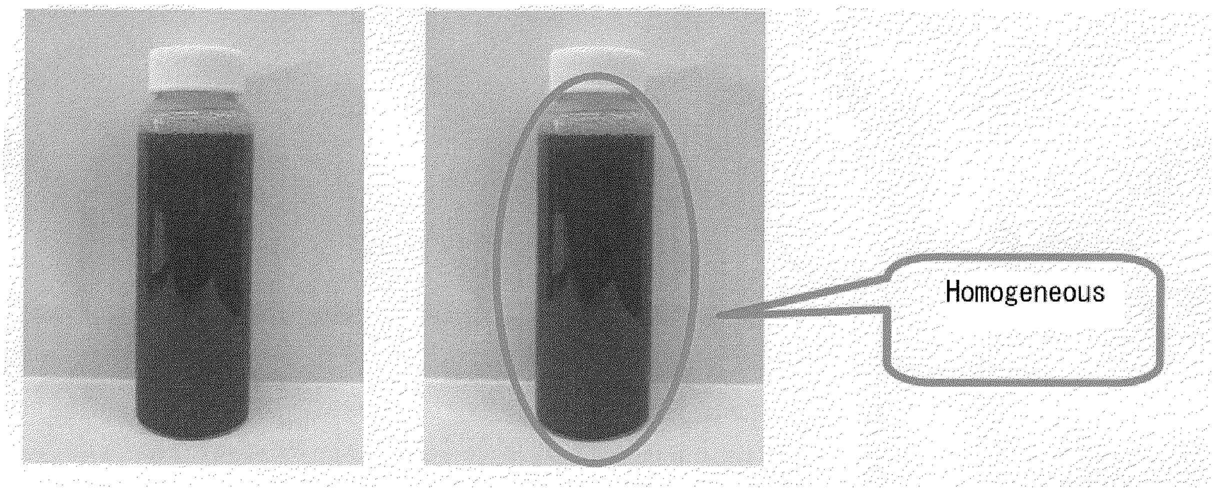
[FIG. 3]



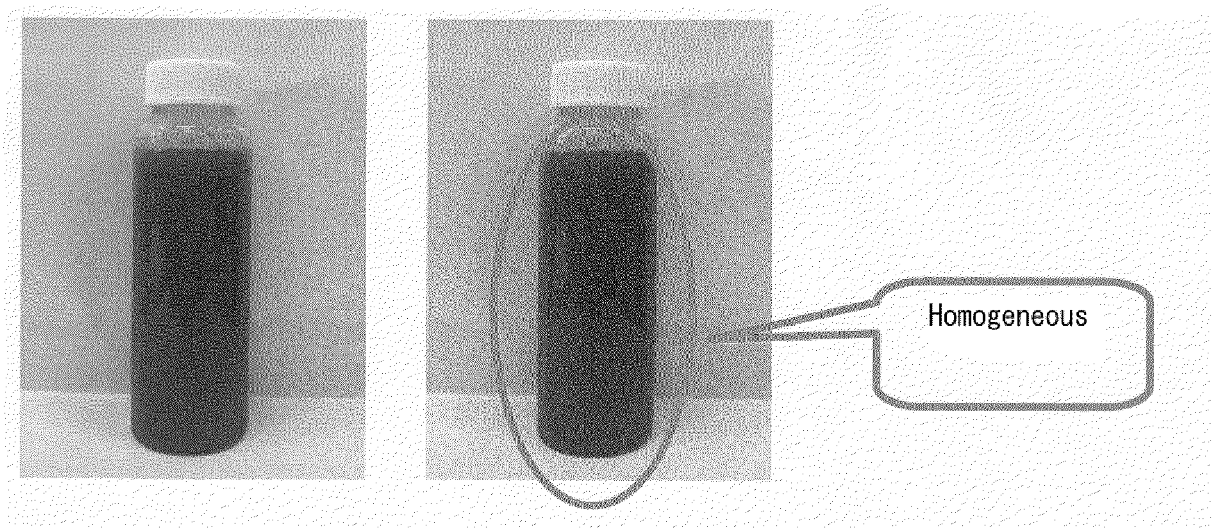
[FIG. 4]



[FIG. 5]



[FIG. 6]



[FIG. 7]

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/020620

A. CLASSIFICATION OF SUBJECT MATTER

C25D 15/02(2006.01)i; *C25D 21/14*(2006.01)n; *C25D 21/18*(2006.01)n
FI: C25D15/02 P; C25D15/02 L; C25D21/14 Z; C25D21/18 G

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)

C25D15/02; C25D21/14; C25D21/18

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
A	Microfilm of the specification and drawings annexed to the request of Japanese Utility Model Application No. 88046/1976 (Laid-open No. 7416/1978) (SUZUKI MOTOR CO., LTD.) 23 January 1978 (1978-01-23)	1-6
A	JP 2011-149071 A (EYETEC CO LTD) 04 August 2011 (2011-08-04)	1-6

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **19 July 2022**	Date of mailing of the international search report **02 August 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/020620

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 53-7416 U1	23 January 1978	(Family: none)	
JP 2011-149071 A	04 August 2011	CN 102753734 A WO 2011/089933 A1	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP H03291395 A **[0008]**
- JP H04371597 A **[0008]**

Non-patent literature cited in the description

- Electroplating & Chemical Plating Guide Book. Tokyo Plating Material Cooperative Association, 1987, 151 **[0009]**