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(54) PALLADIUM PLATING SOLUTION

(57) The present invention provides a palladium plating solution capable of forming a high-purity stable palladium deposit comprising a plated film having a thickness of 5 μm and free from cracks.

The palladium plating solution contains 0.1 to 40.0 g/l of a soluble palladium salt in terms of palladium, 0.01 to 10 g/l of pyridine carboxylic acid and/or 0.002 to 1.0 g/l of at least one salt selected from the group consisting of soluble iron, zinc, thallium, selenium and tellurium salts in terms of metal, 0.005 to 10 g/l of an amine derivative of pyridine carboxylic acid, and 0.001 to 1.2 g/l of an aldehydebenzoic acid derivative and 0.001 to 1.2 g/l of an anionic surfactant or an ampholytic surfactant.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a palladium plating solution, and particularly, to a palladium plating solution suitable to provide a palladium-plated ornamental material in which a nickel allergy problem associated with an ornamental material has been solved.

BACKGROUND ART

[0002] Palladium plating solutions have been studied in a wider range from old. A deposit resulting from the plating has excellent physical properties, e.g., is excellent in light resistance, corrosion resistance, discoloration resistance, wear resistance and the like. Therefore, palladium plating solutions have been used in applications in a wider field such as an ornamental material, an electric contact of an electronic part, a connector, a circuit board and the like. To subject a personal ornament such as a watch case, a watch band, an eyeglass frame, a necklace, an ear-ring and a finger ring to a white plating by a conventional surface-treating technique, in general, a palladium plating, a palladium-nickel alloy plating, a palladium-cobalt alloy plating, a rhodium plating, a platinum plating, a silver plating and the like are carried out.

[0003] The above plating processes suffer the following disadvantages: The rhodium plating is not of practical use, because it is very expensive. In the silver plating, a plated material is liable to be discolored due to a resulting sulfide. In the palladium-nickel alloy plating, a nickel allergy may be produced in some cases and for this reason, the use of the palladium-nickel alloy plating is prohibited in Europe. In the palladium plating and the platinum plating, a resulting film has a high stress and for this reason, if a film is formed at a large thickness, the film is liable to be cracked.

[0004] There are conventionally proposed plating processes suitable for reducing the internal stress in the palladium deposit or for improving the gloss of a film in consideration of the above disadvantages. In one of the proposed plating processes, any of sulfite, nitrous acid and sodium and potassium salts thereof is incorporated in a plating solution (see Japanese Patent Publication No.1-47557). In the other proposed plating process, cerium is incorporated in a plating solution (see Japanese Patent Application Laid-open No.2-43393). Even in such conventional surface-treating technique, however, the cracking problem due to the internal stress in the thick palladium deposit or a practical subject for maintaining the appearance gloss could not be solved sufficiently.

[0005] Recently, various ornamental materials made by the palladium plating are complicated considerably in shapes. Therefore, it is required that a palladium deposit put into a processing or working is excellent in extensibility, and that no crack is produced in a moderately bending treatment.

[0006] For ornaments such as a watchcase, a watchband, an eyeglass frame, a necklace, an ear-ring and a finger ring for Europe, a palladium plating solution capable of forming a high-purity stable and thick deposit is required as a white metal plating solution capable of preventing the occurrence of the nickel allergy.

[0007] Accordingly, it is an object of the present invention to provide a palladium plating solution from which a palladium deposit exhibiting high-purity stable physical properties can be formed.

DISCLOSURE OF THE INVENTION

[0008] The present inventors has made zealous repeated studies to provide a palladium plating solution which can be practically used even in an industrial scale and which is capable of forming a high-purity palladium deposit, with the above circumstance in view, and as a result, they have found that a palladium plating solution produced by incorporating a soluble palladium salt, pyridine carboxylic acid and/or the soluble trace metal salt thereof, an amide derivative of pyridine carboxylic acid and an anionic surfactant or an ampholytic surfactant exhibits a moderate depositing speed and is excellent in stability, and produces a high-purity palladium deposit film, which has a thickness equal to or larger than 5 μm, which is excellent in specular gloss and in which cracks are little produced. Thus, the present invention has been accomplished.

[0009] The present invention provides

(1) a palladium plating solution comprising 0.1 to 40.0 g/l of a soluble palladium salt in terms of palladium, 0.01 to 10 g/l of pyridine carboxylic acid and/or 0.002 to 1.0 g/l of at least one salt selected from the group consisting of soluble iron, zinc, thallium, selenium and tellurium salts in terms of metal, 0.005 to 10 g/l of an amine derivative of pyridine carboxylic acid, and 0.001 to 1. 2 g/l of an aldehydebenzoic acid derivative and 0.001 to 1.2 g/l of an anionic surfactant or an ampholytic surfactant;

(2) a palladium plating solution according to claim 1, wherein the soluble palladium salt is at least one selected from the group consisting of palladium chloride, dichlorodiamine palladium and dichlorotetraamine palladium;

(3) a palladium plating solution according to claim 1, wherein the pyridine carboxylic acid is at least one selected from the group consisting of nicotinic acid, picolinic acid, iso-nicotinic acid, 2,3-quinolinic acid, 2,4-lutidinic acid and 2,6-dipicolinic acid;

(4) a palladium plating solution according to claim 1, wherein each of the soluble, iron, zinc, thallium, selenium and tellurium salts is at least one selected from the group consisting of ferric or ferrous sulfate, ferrous ammonium sulfate, zinc sulfate, thallium sulfate, thallium acetate, selenic acid, selenious acid, sodium selenite and potassium selenite;

(5) a palladium plating solution according to claim 1, wherein the amine derivative of the pyridine carboxylic acid is at least one selected from the group consisting of nicotinamide, picolinamide, iso-nicotinic acid amide, and nicotinic acid amide;

(6) a palladium plating solution according to claim 1, wherein the aldehydebenzoic acid derivative is at least one selected from the group consisting of p-phthalaldehyde, o-phthalaldehyde, o-phthalaldehydic acid, p-phthalaldehydic acid, m-phthalaldehyde, iso-phthalaldehydic acid and phthalaldehyde ammonium;

(7) a palladium plating solution according to claim 1, wherein the anionic surfactant or the ampholytic surfactant is at least one selected from the group consisting of dodecylamine acetate, cetylpyridium bromide, di-2-ethylhexyl sodium sulfosuccinate, sorbitan monopalmitate, polyoxyethylene stearate, sorbitan monostearate, dimethylalkyl betaine and dodecyltrimethyl ammonium chloride and polyoxyethylene sorbitan monopalmitate;

(8) a palladium plating solution according to any of claims 1 to 7, wherein the palladium plating solution contains a conductive salt which is at least one selected from the group consisting of ammonium nitrate, ammonium sulfate, ammonium chloride, ammonium sulfamate, boric acid, ammonium borate, potassium nitrate, potassium sulfate, potassium chloride and potassium sulfamate.

BEST MODE FOR CARRYING OUT THE INVENTION

[0010] Examples of the soluble palladium salt used in the present invention are palladium chloride, dichlorodiamine palladium, dichlorotetraamine palladium and the like. These salts may be used alone or in combination of two or more. The concentration of the soluble palladium salt in the palladium plating solution is preferable to be in a range of 1.0 to 40.0 g/l in terms of palladium. If the concentration is equal to or smaller than 1.0 g/l, a film-depositing speed is lower and hence, such concentration is not preferred. If the concentration is equal to or larger than 40.0 g/l, the forming speed cannot be increased and hence, such concentration is not of practical use.

[0011] Examples of the pyridine carboxylic acid are nicotinic acid, picolinic acid, iso- nicotinic acid, 2, 3-quinolinic acid, 2,4-lutidinic acid and 2,6-dipicolinic acid. These pyridine carboxylic acids may be used alone or in combination of two or more.

[0012] The concentration of the pyridine carboxylic acid in the palladium plating solution is in a range of 0.01 to 20.0 g/l, preferably in a range of 1.0 to 10.0 g/l. If the concentration is equal to or smaller than 0.01 g/l, a gloss-enhancing effect is not provided. If the concentration is equal to or larger than 20.0 g/l, the gloss cannot be enhanced and hence, such concentration is not of practical use.

[0013] According to the present invention, to reduce the internal stress in the palladium deposit, the soluble metal salt is used in combination with the pyridine carboxylic acid or in place of the pyridine carboxylic acid. The soluble metal salt may be, for example, any of soluble iron, thallium, selenium and tellurium salts. Particular examples of the soluble metal salt are ferric or ferrous sulfate, ferrous ammonium sulfate, zinc sulfate, thallium sulfate, thallium acetate, selenic acid, selenious acid, sodium selenite, potassium selenite and the like. The soluble metal salts may be used alone or in combination of two or more.

[0014] The concentration of the soluble metal salt is in a range of 0.002 to 1.0 g/l, preferably, in a range of 0.005 to 0.7 g/l in terms of metal. If the concentration of the soluble metal salt is equal to or smaller than 0.002 g/l, an effect of reducing the internal stress in the palladium deposit is not provided. On the other hand, if the concentration is equal to or larger than 1. 0 g/l, the internal stress in the palladium deposit cannot be increased, and hence, such concentration is not of practical use.

[0015] Examples of the amide derivative of the pyridine carboxylic acid are nicotinamide, picolinamide, iso-nicotinic acid amide, nicotinic acid amide and the like. These amide derivatives of the pyridine carboxylic acids may be used alone or in combination of two or more. The concentration of the amide derivative of the pyridine carboxylic acid in the palladium plating solution is in a range of 0.002 to 20.0 g/l, preferably, in a range of 0.005 to 10.0 g/l. If the concentration of the amide derivative is equal to or smaller than 0.002 g/l, a gloss-enhancing effect is not provided, and even if the concentration of the amide derivative exceeds 20.0 g/l, the gloss cannot be enhanced and hence, concentration exceeding 20.0 g/l is not of practical use.

[0016] Further, examples of the aldehydebenzoic acid derivative are p-phthalaldehyde, o-phthalaldehyde, o-phthalaldehydic acid, p-phthalaldehydic acid, m-phthalaldehyde, iso-phthalaldehydic acid and aldehyde ammonium. The aldehydobenzoic acid derivatives may be used alone or in combination of two or more.

[0017] The concentration of the aldehydebenzoic acid derivative in the palladium plating solution is in a range of 0. 002 to 20. 0 g/l, preferably, in a range of 0.005 to 10.0 g/l. If the concentration of the aldehydebenzoic acid derivative is equal to or smaller than 0.002 g/l, a gloss-enhancing effect is not provided. Even if the concentration of the aldehydebenzoic acid derivative exceeds 20.0 g/l, the gloss cannot be enhanced and hence, the concentration exceeding 20.0 g/l is not of practical use.

[0018] Further, the anionic surfactant or the ampholytic surfactant used in the present invention is used to prevent the pitting, and most effective for an ornament material of a complicated shape. Particular examples of the anionic surfactant or the ampholytic surfactant are dodecylamine acetate, cetylpyridium bromide, di-2-ethylhexyl sodium sulfosuccinate, sorbitan monopalmitate, polyoxyethylene stearate, sorbitan monostearate, dimethylalkyl betaine and dodecyltrimethyl ammonium chloride, polyoxyethylene sorbitan monopalmitate. The anionic surfactants or the ampholytic surfactants may be used alone or in combination of two or more.

[0019] The concentration of the anionic surfactant or the ampholytic surfactant in the palladium plating solution is in a range of 0.001 to 1.2 g/l.

[0020] The concentration of the surfactant equal to or smaller than 0.001 g/l is not sufficient to prevent the pitting, and even if the concentration of the surfactant equal to or larger than 1.2 g/l is used, the prevention of the pitting cannot be enhanced and hence, the concentration of the surfactant equal to or larger than 1.2 g/l is not of practical use.

[0021] According to the present invention, any of potassium phosphate, potassium hydrogen phosphate, ammonium hydrogen phosphate, ammonium chloride, ammonium sulfate, boric acid, ammonium borate, ammonium nitrate, ammonium sulfamate, potassium nitrate, potassium sulfate, potassium chloride, potassium sulfamate and the like may be added to the plating solution in order to provide a conductivity and a buffering property to the plating solution. These additives may be used alone or in combination of two or more.

[0022] The concentration of the conductive salt in the plating solution is in a range of 15.0 to 300. 0 g/l. If the concentration of the conductive salt is equal to or smaller than 15.0 g/l, the conductivity of the plating solution is poor. If the concentration of the conductive salt is equal to or larger than 300.0 g/l, the specific gravity of the plating solution is increased, and a tarnishing, a fogging, a scorching or the like is produced and hence, the concentration equal to or larger than 300.0 g/l is not preferred.

[0023] The plating solution according to the present invention is used at pH in a range of 7 to 12, preferably, in a range of 7.5 to 9.5. In this pH range, a good plated film can be formed. The pH value of the plating solution is adjusted using an acid such as hydrochloric acid and sulfuric acid, or an alkaline substance such as sodium hydroxide, potassium hydroxide and ammonia water.

[0024] The plating solution according to the present invention can be used in a plating treatment at a temperature in a range of 30 to 55°C. Particularly, when the temperature of the plating solution is in a range of 40 to 55°C, a smooth, glossy good plated film can be formed. As the temperature of the plating solution is higher, the film-depositing speed tends to be higher. Any film-depositing speed can be provided by setting the temperature of the plating solution at an appropriate value in the above-described range. Further, in the plating solution according to the present invention, the film-depositing speed depends on the concentration of palladium in addition to the temperature of the plating solution. Therefore, the film-depositing speed can be also regulated by setting the concentration of palladium at an appropriate value and hence, it is easy to control the thickness of the plated film.

[0025] The current density for the plating treatment is in a range of 0.3 to 1.2 A/dm^2.

EXAMPLES

[0026] The present invention will now be described in detail by way of Examples.

Example 1

[0027]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Tellurous acid	0.05 g/l (in terms of Te)
Ammonium chloride	80 g/l
Ammonium hydrogen phosphate	20 g/l
Nicotinic acid amide	0.8 g/l
Di-2-ethylhexyl sodium sulfosuccinate	0.01 g/l

[0028] The plating solution was regulated to pH of 8.3 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 45°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed.

Example 2

[0029]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Ammonium chloride	90 g/l
Boric acid	10 g/l
Nicotinamide	1.0 g/l
2,6-dipicolinic acid	0.5 g/l
Dodecyl trimethyl ammonium chloride	0.1 g/l

[0030] The plating solution was regulated to pH of 8.3 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 42°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed.

Example 3

[0031]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Ferrous ammonium sulfate	0.1 g/l (in terms of Fe)
Ammonium chloride	90 g/l
Boric acid	10 g/l
Nicotinamide	1.0 g/l
2,6-dipicolinic acid	0.5g/l
Dodecyltrimethyl ammonium chloride	0.1 g/l

[0032] The plating solution was regulated to pH of 8.3 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 42°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed.

Example 4

[0033]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Ammonium sulfate	60 g/l
Boric acid	20 g/l
Ammonium hydrogen phosphate	30 g/l
Nicotinic acid	1.0 g/l
Picolinamide	0.5 g/l

(continued)

Composition of Plating Solution	
Di-2-ethylhexyl sodium sulfosuccinate	0.1 g/l

[0034] The plating solution was regulated to pH of 8.2 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 50°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed. The palladium-plated film was also subjected to an artificial sweat immersion test (for 48 hours in room temperature) and as a result, the discoloration was not observed.

Example 5

[0035]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Thallium sulfate	0.035 g/l (in terms of T1)
Ammonium sulfate	60 g/l
Boric acid	20 g/l
Ammonium hydrogen phosphate	30 g/l
Nicotinic acid	1.0 g/l
Picolinamide	0.5 g/l
Di-2-ethylhexyl sodium sulfosuccinate	0.1 g/l

[0036] The plating solution was regulated to pH of 8.2 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 50°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed. The palladium-plated film was also subjected to an artificial sweat immersion test (for 48 hours in room temperature) and as a result, the discoloration was not observed.

Example 6

[0037]

Composition of Plating Solution	
Dichlorodiamine palladium	10 g/l (in terms of Pd)
Ammonium chloride	40 g/l
Ammonium sulfate	20 g/l
Nicotinic acid	0.5 g/l
Iso-nicotinic acid amide	0.2 g/l
Di-2-ethylhexyl sodium sulfosuccinate	0.1 g/l

[0038] The plating solution was regulated to pH of 8.5 by ammonia water, and a previously nickel-plated brass plate having a size of 25 x 35mm was immersed in the plating solution at a bath temperature of 50°C and at a current density of 1.0 A/dm^2 for 30 minutes. As a result, a glossy palladium-plated film having an average thickness of 7 μm was produced. The palladium-plated film was subjected to an ammonia exposure test (for 12 hours at room temperature) and as a result, the generation of cracks was not observed.

Comparative Example 1

[0039] A palladium plating solution having a composition made by removing the tellurous acid and nicotinic acid

amide from the palladium plating solution used in Example 1 and adding 1.0 g/l of EDTA in place of these acids was used to carry out a plating treatment under the same conditions as in Example 1. A produced palladium plated film was subjected to an ammonia exposure test and as a result, cracks were produced in 6 hours at room temperature.

Comparative Example 2

[0040] A palladium plating solution having a composition made by removing the nicotinamide from the palladium plating solution used in Example 2 was used to carry out a plating treatment under the same conditions as in Example 2. A produced palladium plated film was ununiform and had not a gloss.

Comparative Example 3

[0041] A palladium plating solution having a composition made by removing the ferrous ammonium sulfate and the nicotinamide from the palladium plating solution used in Example 3 and adding 1.0 g/l of EDTA in place of these substances was used to carry out a plating treatment under the same conditions as in Example 3. A produced palladium plated film was subj ected to an ammonia exposure test and as a result, cracks were produced in 6 hours at room temperature.

Comparative Example 4

[0042] A palladium plating solution having a composition made by removing the nicotinic acid from the palladium plating solution used in Example 6 was used to carry out a plating treatment under the same conditions as in Example 6. A produced palladium plated film was ununiform and had not a gloss.

Industrial Applicability

[0043] As discussed above, the palladium plating solution according to the present invention has an extremely good can-stability and exhibits a good workability and a good working environment. The depositing speed depends on the concentration of palladium and the temperature of the plating solution and hence, it is easy to control the thickness of the plated film. Even if the film formed by the plating solution according to the present invention has a thickness of 5 μm or more, it has a gloss, a lower stress, no crack produced and an excellent extensibility, and presents a beautiful white specular gloss. Even in the ammonia exposure test of the plated film for 12 hours at room temperature, no crack is produced. In the test in which the plated film is entirely or partially immersed in an artificial sweat for 48 hours at room temperature, the discoloration does not occur and thus, an excellent palladium film can be produced.

Claims

1. A palladium plating solution comprising 0.1 to 40.0g/l of a soluble palladium salt in terms of palladium, 0.01 to 10g/l of pyridine carboxylic acid, 0.005 to 10g/l of an amine derivative of pyridine carboxylic acid and 0.001 to 1.2g/l of an anionic or an ampholytic surfactant, **characterised by** the presence of 0.002 to 1.0g/l of at least one salt selected from soluble iron, zinc, thallium, selenium and tellurim in terms of metal and 0.001 to 1.2g/l of an aldehydebenzoic acid derivative.

2. A palladium plating solution according to claim 1, wherein said soluble palladium salt is at least one selected from palladium chloride, dichlorodiamine palladium and dichlorotetraamine palladium.

3. A palladium plating solution according to claim 1, wherein said pyridine carboxylic acid is at least one selected from nicotinic acid, picolinic acid, iso-nicotinic acid, 2,3-quinolinic acid, 2,4-lutidinic acid and 2,6-dipicolinic acid.

4. A palladium plating solution according to claim 1, wherein each of the soluble, iron, zinc, thallium, selenium and tellurium salts is at least one selected from ferric or ferrous sulfate, ferrous ammonium sulfate, zinc sulfate, thallium sulfate, thallium acetate, selenic acid, selenious acid, sodium selenite and potassium selenite.

5. A palladium plating solution according to claim 1, wherein said amine derivative of the pyridine carboxylic acid is at least one selected from nicotinamide, picolinamide, iso-nicotinic acid amide, and nicotinic acid amide.

6. A palladium plating solution according to claim 1, wherein said aldehydebenzoic acid derivative is at least one

selected from p-phthalaldehyde, o-phthalaldehyde, o-phthalaldehydic acid, p-phthalaldehydic acid, m-phthalaldehyde, iso-phthalaldehydic acid and aldehyde ammonium.

7. A palladium plating solution according to claim 1, wherein said anionic surfactant or said ampholytic surfactant is at least one selected from dodecylamine acetate, cetylpyridium bromide, di-2-ethylhexyl sodium sulfosuccinate, sorbitan monopalmitate, polyoxyethylene stearate, sorbitan monostearate, dimethylalkyl betaine and dodecyltrimethyl ammonium chloride and polyoxyethylene sorbitan monopalmitate.

8. A palladium plating solution according to any of claims 1 to 7, wherein said palladium plating solution contains a conductive salt which is at least one selected from ammonium nitrate, ammonium sulfate, ammonium chloride, ammonium sulfamate, boric acid, ammonium borate, potassium nitrate, potassium sulfate, potassium chloride and potassium sulfamate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/05107

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl[7] C25D3/50

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[7] C25D3/50

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001
Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001

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.
EX	JP 2001-192885 A (Kojima Kagaku Yakuhin K.K.), 17 July, 2001 (17.07.01), Claims (Family: none)	1-8
X	JP 7-11476 A (Kojima Kagaku Yakuhin K.K.), 13 January, 1995 (13.01.95), Claims (Family: none)	1,3,5,7,8
Y		2,4
Y	JP 7-278870 A (Kojima Kagaku Yakuhin K.K.), 24 October, 1995 (24.10.95), Par. No. [0005] (Family: none)	2
Y	JP 2000-303199 A (Nisshin Kasei K.K.), 31 October, 2000 (31.10.00), Par. Nos. [0024], [0043] to [0047] (Family: none)	2,4
A	US 4911799 A (AT & T), 27 March, 1990 (27.03.90), Claims 1, 3, 9, 15 & JP 3-90590 A & EP 415631 A1	2,3,7,8

☒ 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
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"&" *document member of the same patent family*

Date of the actual completion of the international search	Date of mailing of the international search report
27 August, 2001 (27.08.01)	04 September, 2001 (04.09.01)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP01/05107

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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A	US 4491507 A (W. C. Heraeus GmbH), 01 January, 1985 (01.01.85), Claim 1 & JP 59-211588 A & DE 3317493 A	5
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)