

(19)



(11)

**EP 4 484 608 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**01.01.2025 Bulletin 2025/01**

(51) International Patent Classification (IPC):  
**C23C 18/36<sup>(2006.01)</sup> C23C 18/16<sup>(2006.01)</sup>**

(21) Application number: **24183271.6**

(52) Cooperative Patent Classification (CPC):  
**C23C 18/36; C23C 18/1653**

(22) Date of filing: **20.06.2024**

(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 ME MK MT NL  
NO PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA**  
Designated Validation States:  
**GE KH MA MD TN**

(71) Applicant: **Ricoh Company, Ltd.**  
**Tokyo 143-8555 (JP)**

(72) Inventors:  
• **SAITO, Akira**  
**Tokyo, 143-8555 (JP)**  
• **OZAKI, Daisuke**  
**Tokyo, 143-8555 (JP)**

(30) Priority: **30.06.2023 JP 2023108505**

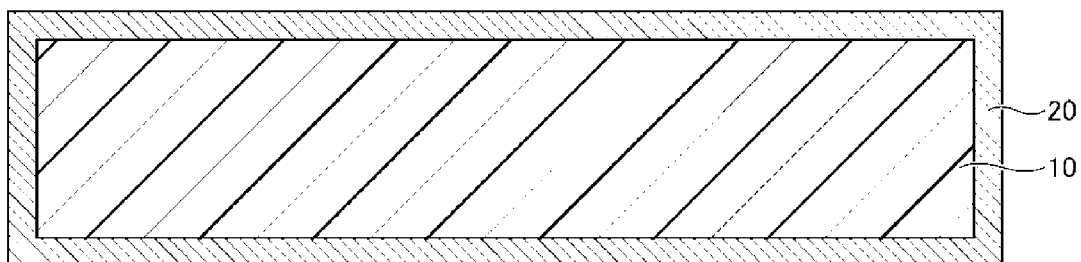
(74) Representative: **Marks & Clerk LLP**  
**15 Fetter Lane**  
**London EC4A 1BW (GB)**

(54) **RESIN-METAL COMPOSITE BODY AND METHOD OF MANUFACTURING RESIN-METAL COMPOSITE BODY**

(57) A resin-metal composite body (100) is provided that includes a resin base material (10) having a surface roughness Sq of 1.5  $\mu\text{m}$  or more and a surface roughness

Sku of 4.5  $\mu\text{m}$  or less, and a metal plating (20) on the resin base material (10).

100



**EP 4 484 608 A1**

## Description

### BACKGROUND

#### 5 Technical Field

**[0001]** The present disclosure relates to a resin-metal composite body and a method of manufacturing a resin-metal composite body.

#### 10 Related Art

**[0002]** A technique for decorating a surface of a base material formed of a resin (may be referred to as "resin base material" hereinafter) by plating the surface with a metal (see, for example, Japanese Unexamined Patent Application Publication No. 2008-290295) has been proposed.

**[0003]** However, a metal plating treatment of a resin base material for decorative purposes does not anticipate exposure of the resin base material to strong impacts. In particular, even when components used in industrial water turbines are subjected to a metal plating treatment of a resin base material for decorative purposes, there is a problem that the metal plating may peel off due to an impact such as a water current.

### 20 SUMMARY

**[0004]** In view of the above-described problems, an object of the present invention is to provide a resin-metal composite body in which the adhesion between a resin base material and a metal plating is excellent and by which it is possible to improve the strength of the resin base material.

**[0005]** A resin-metal composite body according to embodiments of the present invention as a means for solving the above-described problems includes a resin base material having a surface roughness  $S_q$  of  $1.5\ \mu\text{m}$  or more and a surface roughness  $S_{ku}$  of  $4.5\ \mu\text{m}$  or less, and a metal plating on the resin base material.

**[0006]** According to embodiments of the present invention, a resin-metal composite body is provided in which the adhesion between a resin base material and a metal plating is excellent and by which it is possible to improve the strength of the resin base material.

### BRIEF DESCRIPTION OF THE DRAWINGS

**[0007]** A more complete appreciation of embodiments of the present disclosure and many of the attendant advantages and features thereof can be readily obtained and understood from the following detailed description with reference to the accompanying drawing, wherein:

the drawing is a schematic cross-sectional view illustrating a resin-metal composite body according to one embodiment of the present invention.

**[0008]** The accompanying drawing is intended to depict embodiments of the present disclosure and should not be interpreted to limit the scope thereof. The accompanying drawing is not to be considered as drawn to scale unless explicitly noted. Also, identical or similar reference numerals designate identical or similar components throughout the several views.

### DETAILED DESCRIPTION

**[0009]** In describing embodiments illustrated in the drawings, specific terminology is employed for the sake of clarity. However, the disclosure of this specification is not intended to be limited to the specific terminology so selected and it is to be understood that each specific element includes all technical equivalents that have a similar function, operate in a similar manner, and achieve a similar result.

**[0010]** Referring now to the drawings, embodiments of the present disclosure are described below. As used herein, the singular forms "a," "an," and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise.

(Resin-Metal Composite Body)

**[0011]** The drawing is a schematic cross-sectional view illustrating a resin-metal composite body according to one embodiment of the present invention. A resin-metal composite body 100 illustrated in the drawing includes a resin base material 10 and a metal plating 20 on the resin base material.

<Resin Base Material>

**[0012]** In the resin base material, a base material surface (that is, an interface between the resin base material 10 and the metal plating 20) has a surface roughness Sq of 1.5 μm or more and a surface roughness Sku of 4.5 μm or less. The resin base material preferably has a surface roughness Sq of 1.5 μm or more and 20 μm or less and a surface roughness Sku of 1.0 μm or more and 4.5 μm or less. When the surface roughness Sq is 1.5 μm or more and the surface roughness Sku is 4.5 μm or less, the adhesion between the resin base material and the metal plating is excellent.

**[0013]** The surface roughness Sq corresponds to the standard deviation of the height in an area of a defined region, and is defined by Equation (1) below.

$$Sq = \sqrt{\frac{1}{A} \iint_A z^2(x, y) dx dy} \quad \dots \text{Equation (1)}$$

**[0014]** (in Equation (1) above, A represents the area of the defined region, x represents the x-axis coordinate, y represents the y-axis coordinate, and z represents the z-axis coordinate)

**[0015]** The surface roughness Sku indicates the sharpness of the height distribution in the area of a defined region, and is defined by Equation (2) below.

$$Sku = \frac{1}{Sq^4} \left[ \frac{1}{A} \iint_A z^4(x, y) dx dy \right] \quad \dots \text{Equation (2)}$$

(in Equation (2) above, A represents the area of the defined region, x represents the x-axis coordinate, y represents the y-axis coordinate, and z represents the z-axis coordinate)

**[0016]** A method of measuring the surface roughness Sq and the surface roughness Sku is not particularly limited and can be appropriately selected according to a purpose. For example, an image of a surface of the resin base material may be obtained by performing an Opt-SEM measurement at a magnification of 1,500 times in a high image quality depth synthesis mode using an electron microscope (Keyence Corporation VHX7000), and the analysis software of the electron microscope may be used to calculate the surface roughness of all regions in the obtained image.

**[0017]** The resin base material is preferably not subjected to an acid treatment or a blast treatment, but may be subjected to a surface treatment, if desired.

**[0018]** The resin base material contains a resin and a filler, and may further contain other components, if desired.

- Resin -

**[0019]** The resin is not particularly limited and can be appropriately selected according to a purpose. Examples of the resin include, but are not limited to, thermoplastic resins, thermosetting resins, photocurable resins, recycled plastics, and bioplastics.

**[0020]** The recycled plastics mentioned above are plastics prepared by reusing plastics that were discarded after use. Recycled plastics are the oldest environmentally friendly plastics, and many products are already made from recycled plastics.

**[0021]** The two main technologies for producing recycled plastics are "material recycling" and "chemical recycling".

**[0022]** Material recycling is a technology that uses used plastics as raw materials to create new products. For example, used PET bottles are collected and sorted, then crushed, washed, and processed to remove foreign matter to turn the bottles into recycled plastic referred to as flakes or pellets. This recycled plastic can be used to produce other plastic products such as trays and films, or turned into fibers to produce clothing. However, recycled plastic obtained by material recycling tends to have lower quality than new plastic, and also has the disadvantage of having limited uses.

**[0023]** Chemical recycling is a technology that chemically breaks down used plastics and returns the used plastic to petroleum-based raw materials and monomers, to produce plastic raw materials equivalent to new plastics. Chemical recycling is a newer technology than material recycling, and has the excellent feature of offering the possibility for

recycling, even if different types of plastics are mixed together or if foreign matter or dirt are present. As a result of developing the technology of chemical recycling, it has become possible to realize the "bottle-to-bottle" process, in which new PET bottles are produced from used PET bottles.

**[0024]** The recycled plastics are not particularly limited and can be appropriately selected according to a purpose.

Examples of the recycled plastics include, but are not limited to, polyethylene (PE), polypropylene (PP), an ethylene-propylene copolymer, polybutadiene, an acrylonitrile-butadiene-styrene copolymer (ABS), polystyrene (PS), acrylonitrile-chlorinated polyethylene-styrene copolymer resin (ACS), acrylonitrile-styrene copolymer resin (AS), polybutene resin, alkyd resins, amino resins, acrylonitrile-acrylic rubber-styrene copolymer resin (ASA), bismaleimide triazine resin, chlorinated polyether, chlorinated polyethylene, allyl resins, epoxy resins, ethylene- $\alpha$ -olefin copolymers, an ethylene-vinyl acetate-vinyl chloride copolymer, an ethylene-vinyl chloride copolymer, ethylene-vinyl alcohol resin (EVA), ionomers, methacrylic-styrene copolymers, nitrile resin, polyesters [such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT)], olefin-vinyl alcohol copolymers, petroleum resins, phenol resins, polyacetal, polyacrylates, polyamides, polyarylsulfones, polybenzimidazole, polybutylene, polycarbonates, polyether ether ketone, polyether ketone, polyether nitrile, polyether sulfone, polyketone, methacrylic resin, polymethylpentene, polyphenylene ethers, polyphenylene sulfides, polysulfones, butadiene-styrene resin, polyurethane, polyvinyl acetal, polyvinyl alcohol, polyvinyl chloride, polyvinylidene chloride, silicone resins, polyvinyl acetate, xylene resins, crosslinked polyolefins such as crosslinked polyethylene, crosslinked polystyrene, unsaturated polyester resins, urea resin, melamine resin, fluororesins, biodegradable resins, thermoplastic elastomers, and an ethylene-propylene-diene copolymer (EPDM).

**[0025]** The term bioplastics is a general term used for plastics obtained by using biomass as a raw material (biomass plastics) and plastics having biodegradability (biodegradable plastics). However, not every plastic derived from biomass is biodegradable, and conversely, not every plastic that is biodegradable is a plastic whose raw material is biomass.

**[0026]** The biomass plastics mentioned above are plastics obtained by using biological resources (biomass), which are renewable resources, as a raw material. Methods of synthesizing biomass plastics are broadly divided into two types. The first type of methods uses starch or sugar derived from corn or sugar cane as raw materials, and transforms the starch or the sugar into a different substance by fermentation or other processes, to synthesize a monomer, and then, polymerizes the monomer to obtain a polymer. Examples of the polymer include, but are not limited to, polylactic acid (PLA), which is a polymer of lactic acid, and polyhydroxyalkanoate (PHA) produced by microorganisms. The second type of methods extracts polysaccharides such as cellulose from plants and the like, and then, forms a derivate of the polysaccharides while using the structure of the polymer backbone of the polysaccharide to obtain a thermoplastic material (such as cellulose acetate).

**[0027]** Polymers obtained by using biomass as a raw material (mainly cellulose derivatives such as nitrocellulose) have been widely studied even before the synthesis of polymers derived from fossil resources. However, from the first half of the 20th century, highperformance polymers derived from fossil resources started being produced at low cost and in large quantities (such as nylon and polypropylene), and research into materials made from biomass decreased. Due to growing social awareness of the environment, since the latter half of the 20th century, attention returned to materials produced by using biomass as a raw material.

**[0028]** The biodegradable plastics refer to plastics that can be used similarly to normal plastic, and after use, are ultimately decomposed into water and carbon dioxide by the action of microorganisms present in nature.

**[0029]** Biodegradable plastics include plastics derived from biological resources (biomass) (biomass plastics) and plastics derived from petroleum (synthetic petroleum plastics). As long as the plastic is biodegradable, any raw material may be used. The most widely used biodegradable plastic is biomass plastic, which is produced by using biological resources (biomass) as a raw material, and many of the biomass plastics are made from starch or sugar. However, not all plastics produced from biomass are biodegradable. For example, bio-PET and bio-PE are made from biomass, but are not biodegradable.

**[0030]** Major biodegradable plastics produced by using biomass as a raw material include, but are not limited to, polylactic acid, polycaprolactone, polyhydroxyalkanoates (PHAs, microbial polyesters), polyglycolic acid, modified polyvinyl alcohol, casein, modified starch, and low-substituted polysaccharide derivatives (such as low-substituted cellulose acetate). Examples of petroleum-derived plastics include, but are not limited to, PET copolymers.

- Filler -

**[0031]** The filler can be appropriately selected in accordance with the desired physical properties to be improved. However, fillers in the form of fibers such as cellulose nanofibers, glass fibers, and bismaleimide resin are preferred. By using a filler in the form of fibers such as cellulose nanofibers, glass fibers, and bismaleimide resin as the filler, it is possible to achieve a surface roughness  $S_q$  of  $1.5\text{ }\mu\text{m}$  or more and a surface roughness  $S_{ku}$  of  $4.5\text{ }\mu\text{m}$  or less, without subjecting the resin base material to a surface treatment.

**[0032]** Examples of the filler include, but are not limited to, commercially available fillers such as CELLENPIA (manufactured by Nippon Paper Industries Co., Ltd.), SENAF (manufactured by Hattori Shoten Co., Ltd.), SS05-413

(manufactured by Nitto Boseki Co., Ltd.), BMI-TMH (manufactured by Daiwa Kasei Industrial Co., Ltd.), SC-5500 (manufactured by Admatechs Co., Ltd.), and PBT (manufactured by Ricoh Co., Ltd.).

#### - Other Components -

**[0033]** The other components are not particularly limited, can be appropriately selected according to a purpose, and examples thereof include a pigment dispersion.

**[0034]** The shape, the size, and the like of the resin base material 10 are not particularly limited and can be appropriately selected according to a purpose. The metal plating 20 is formed on the surface of the resin base material 10, and thus, the shape and the size of the resin base material 10 are substantially the same as the shape and the size of the resin-metal composite body 100. Therefore, the shape and the size of the resin base material 10 can be selected in accordance with an intended purpose of a resin-metal composite body 100 and the like.

**[0035]** A method of forming the resin base material 10 is not particularly limited and can be appropriately selected according to a purpose. For example, the resin base material 10 can be formed by molding, cutting, and further, by using an ultraviolet-curable composition in a 3D printer.

**[0036]** The 3D printer is not particularly limited and can be appropriately selected according to a purpose. Examples of the methods used in the 3D printer include, but are not limited to, fused deposition modeling (FDM), stereolithographic methods, material jet methods, binder jet methods, powder deposition methods, and powder adhesion (bonding) methods. When a 3D printer is used to mold items having a shape that corresponds to the shape of a power generation unit, it is possible to quickly assemble, maintain, inspect, and replace damaged parts of a hydroelectric power generation device.

#### - Ultraviolet-Curable Composition -

**[0037]** The ultraviolet-curable composition (may be referred to as "ink" hereinafter) is not particularly limited and can be appropriately selected according to a purpose. For example, the ultraviolet-curable composition may contain a monomer, an oligomer, a filler, a cross-linking agent, a pigment dispersion, and a polymerization initiator.

**[0038]** The monomer is not particularly limited and can be appropriately selected according to a purpose. For example, commercially available products may be used as the monomer. Examples of commercially available products include, but are not limited to, tricyclodecane dimethanol diacrylate (DCP, manufactured by Shin-Nakamura Chemical Co., Ltd.), hydroxyethyl acrylate (HEA, manufactured by Osaka Organic Chemical Industry Ltd.), VISCOAT #200 (cyclic trimethylolpropane formal acrylate, manufactured by Osaka Organic Chemical Industry Ltd.), phenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, isooctyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, methoxytriethylene glycol (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, ethoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, methoxydixylethyl (meth)acrylate, ethyl diglycol (meth)acrylate, cyclic trimethylolpropane formal mono (meth)acrylate, phenoxyethyl (meth)acrylate, (meth)acrylic acid 2-(2-vinyloxyethoxy)ethyl, tetrahydrofurfuryl (meth)acrylate, imide (meth)acrylate, isoamyl (meth)acrylate, ethoxylated succinic acid (meth)acrylate, trifluoroethyl (meth)acrylate,  $\omega$ -carboxypolycaprolactone mono(meth)acrylate, N-vinylformamide, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, methylphenoxyethyl (meth)acrylate, 4-t-butylcyclohexyl (meth)acrylate, caprolactone-modified tetrahydrofurfuryl (meth)acrylate, tribromophenyl (meth)acrylate, ethoxylated tribromophenyl (meth)acrylate, 2-phenoxyethyl (meth)acrylate, (meth)acryloylmorpholine, phenoxydiethylene glycol (meth)acrylate, vinylcaprolactam, vinylpyrrolidone, 2-hydroxy-3-phenoxypropyl (meth)acrylate, 1,4-cyclohexanedimethanol mono(meth)acrylate, 2-(2-ethoxyethoxy)ethyl (meth)acrylate, stearyl (meth)acrylate, diethylene glycol monobutyl ether (meth)acrylate, lauryl (meth)acrylate, isodecyl (meth)acrylate, 3,3,5-trimethylcyclohexanol (meth)acrylate, isooctyl (meth)acrylate, octyl/decyl (meth)acrylate, tridecyl (meth)acrylate, caprolactone (meth)acrylate, ethoxylated (4) nonylphenol (meth)acrylate, methoxypolyethylene glycol (350) mono(meth)acrylate, methoxypolyethylene glycol (550) mono(meth)acrylate, hexadiol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, polyethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, tripropylene glycol tri(meth)acrylate, neopentyl glycol di(meth)acrylate, bispentaerythritol hexa(meth)acrylate, ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, ethoxylated 1,6-hexanediol di(meth)acrylate, polypropylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, 2-n-butyl-2-ethyl 1,3-propanediol di(meth)acrylate, hydroxypivalic acid neopentyl glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, hydroxypivalic acid trimethylolpropane tri(meth)acrylate, ethoxylated phosphoric acid tri(meth)acrylate, ethoxylated tripropylene glycol di(meth)acrylate, neopentyl glycol-modified trimethylolpropane di(meth)acrylate, stearic acid-modified pentaerythritol di(meth)acrylate, pentaerythritol tri(meth)acrylate, tetramethylolpropane tri(meth)acrylate, tetramethylolmethane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, caprolactone-modified trimethylolpropane tri(meth)acrylate, pro-

poxylated glyceryl tri(meth)acrylate, tetramethylolmethane tetra(meth)acrylate, pentaerythritol tetra(meth)acrylate, di-trimethylolpropane tetra(meth)acrylate, ethoxylated pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol hexa(meth)acrylate, dipentaerythritol hydroxypenta(meth)acrylate, neopentyl glycol oligo(meth)acrylate, 1,4-butanediol oligo(meth)acrylate, hydroxypivalic acid neopentyl glycol (meth)acrylic acid adduct, 1,6-hexanediol oligo(meth)acrylate, trimethylolpropane oligo(meth)acrylate, pentaerythritol oligo(meth)acrylate, ethoxylated neopentyl glycol di(meth)acrylate, propoxylated neopentyl glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, ethoxylated trimethylolpropane tri(meth)acrylate, and propoxylated trimethylolpropane tri(meth)acrylate.

**[0039]** These monomers may be used alone or in combination of two or more types.

**[0040]** The content of the monomer is not particularly limited and can be appropriately selected according to a purpose. However, the content of the monomer is preferably 50 mass% or more and less than 70 mass% with respect to the total amount of the ultraviolet-curable composition.

**[0041]** The oligomer is not particularly limited and can be appropriately selected according to a purpose. For example, commercially available products may be used as the oligomer. Examples of the commercially available products include, but are not limited to, UV-2000B, UV-2750B, UV-3000B, UV-3010B, UV-3200B, UV-3300B, UV-3700B, UV-6640B, UV-8630B, UV-7000B, UV-7610B, UV-1700B, UV-7630B, UV-6300B, UV-6640B, UV-7550B, UV-7600B, UV-7605B, UV-7610B, UV-7630B, UV-7640B, UV-7650B, UT-5449, and UT-5454 manufactured by The Nippon Synthetic Chemical Industry Co., Ltd.; CN104, CN902, CN902J75, CN929, CN940, CN944, CN944B85, CN959, CN961E75, CN961H81, CN962, CN963, CN963A80, CN963B80, CN963E75, CN963E80, CN963J85, CN964, CN965, CN965A80, CN966, CN966A80, CN966B85, CN966H90, CN966J75, CN968, CN969, CN970, CN970A60, CN970E60, CN971, CN971A80, CN971J75, CN972, CN973, CN973A80, CN973H85, CN973J75, CN975, CN977, CN977C70, CN978, CN980, CN981, CN981A75, CN981B88, CN982, CN982A75, CN982B88, CN982E75, CN983, CN984, CN985, CN985B88, CN986, CN989, CN991, CN992, CN994, CN996, CN997, CN999, CN9001, CN9002, CN9004, CN9005, CN9006, CN9007, CN9008, CN9009, CN9010, CN9011, CN9013, CN9018, CN9019, CN9024, CN9025, CN9026, CN9028, CN9029, CN9030, CN9060, CN9165, CN9167, CN9178, CN9290, CN9782, CN9783, CN9788, and CN9893 manufactured by Sartomer Corporation; and EBECRYL 210, EBECRYL 220, EBECRYL 230, EBECRYL 270, KRM8200, EBECRYL 5129, EBECRYL 8210, EBECRYL 8301, EBECRYL 8804, EBECRYL 8807, EBECRYL 9260, KRM7735, KRM8296, KRM8452, EBECRYL 4858, EBECRYL 8402, EBECRYL 9270, EBECRYL 8311, EBECRYL 8701, and EBECRYL 8606 manufactured by Daicel-Cytec Co., Ltd..

**[0042]** These oligomers may be used alone or in combination of two or more types.

**[0043]** It is also possible to synthesize an oligomer instead of using a commercially available product, or to use a combination of a synthesized oligomer and a commercially available oligomer.

**[0044]** The content of the oligomer is not particularly limited and can be appropriately selected according to a purpose. However, the content of the oligomer is preferably 10 mass% or more and 50 mass% or less with respect to the total amount of the ultraviolet-curable composition.

**[0045]** The filler is not particularly limited and can be appropriately selected according to a purpose. For example, a filler similar to those described above can be used.

**[0046]** The content of the filler is not particularly limited and can be appropriately selected according to a purpose. However, the content of the filler is preferably 0.1 mass% or more and 10 mass% or less, and more preferably 0.5 mass% or more and 5 mass% or less, with respect to the total amount of the ultraviolet-curable composition.

**[0047]** The cross-linking agent is not particularly limited and can be appropriately selected according to a purpose. For example, commercially available products can be used as the cross-linking agent. Examples of the commercially available products include, but are not limited to, KBM-503 (manufactured by Shin-Etsu Chemical Co., Ltd.) and KBM-603 (manufactured by Shin-Etsu Chemical Co., Ltd.).

**[0048]** The polymerization initiator is not particularly limited and can be appropriately selected according to a purpose, as long as the polymerization initiator can generate active species such as radicals and cations by the energy of active energy rays and initiate polymerization of a polymerizable compound (a monomer or an oligomer).

**[0049]** Examples of radical polymerization initiators include, but are not limited to, aromatic ketones, acylphosphine oxide compounds, aromatic onium salt compounds, organic peroxides, thio compounds (such as thioxanthone compounds and compounds containing thiophenyl groups), hexaarylbimidazole compounds, ketoxime ester compounds, borate compounds, azinium compounds, metallocene compounds, active ester compounds, compounds having a carbon-halogen bond, and alkylamine compounds.

**[0050]** The above-mentioned radical polymerization initiators may be commercially available products, and examples thereof include, but are not limited to, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (TPO, manufactured by BASF), acetophenone, 2,2-diethoxyacetophenone, p-dimethylaminoacetophenone, benzophenone, 2-chlorobenzophenone, p,p'-chlorobenzophenone, p,p'-bisdiethylaminobenzophenone, Michler's ketone, benzyl, benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin-n-propyl ether, benzoin isobutyl ether, benzoin-n-butyl ether, benzyl methyl ketal, thioxanthone, 2-chlorothioxanthone, 2-hydroxy-2-methyl-1-phenyl-1-one, 1-(4-isopropylphenyl)2-hydro-

xy-2-methylpropan-1-one, methylbenzoyl formate, 1-hydroxycyclohexyl phenyl ketone, azobisisobutyronitrile, benzoyl peroxide, and di-tert-butyl peroxide.

**[0051]** The pigment in the pigment dispersion is not particularly limited and can be appropriately selected according to a purpose. For example, commercially available products can be used as the pigment. Examples of commercially available products include, but are not limited to, Carbon Black #10 (manufactured by Mitsubishi Chemical Group Corporation).

#### <Other Components>

**[0052]** The ultraviolet-curable composition may contain other components, if desired.

**[0053]** The other components are not particularly limited and can be appropriately selected according to a purpose. Examples of the other components include, but are not limited to, a polymerization inhibitor, a coloring material, an organic solvent, a surfactant, a leveling agent, an antifoaming agent, a fluorescent brightening agent, a permeation promoter, a wetting agent (moisturizing agent), a fixing agent, a viscosity stabilizer, an antifungal agent, a preservative, an antioxidant, an ultraviolet absorbing agent, a chelating agent, a pH adjuster, and a thickener.

#### <Metal Plating>

**[0054]** The metal plating is provided on the resin base material to reinforce the resin base material and thus improve the strength of the obtained metal-resin composite body, compared to a case where only the resin base material is used.

**[0055]** The metal plating is not particularly limited and may be appropriately selected according to a purpose. Examples of the metal plating include, but are not limited to, a nickel plating, a copper plating, and a chromium plating. The metal plating may be a plating formed of a single metal, or may have a structure in which a plurality of plating layers formed of different metals are laminated. The metal plating preferably includes at least any one among a nickel plating, a copper plating, and a chromium plating.

**[0056]** The film thickness of the metal plating (that is, the total film thickness of the plurality of layers in the case of a structure in which a plurality of layers are laminated) can be appropriately selected according to a purpose. However, to assure the strength of the metal-resin composite body, the film thickness of the metal plating is preferably 10  $\mu\text{m}$  or more, more preferably 20  $\mu\text{m}$  or more, and even more preferably 50  $\mu\text{m}$  or more. The film thickness of the metal plating is preferably 1,000  $\mu\text{m}$  or less, more preferably 500  $\mu\text{m}$  or less, and even more preferably 300  $\mu\text{m}$  or less, to assure adhesion between the resin base material and the metal plating. Therefore, a suitable range of the film thickness of the metal plating may be a range obtained by freely selecting and combining the above-mentioned lower limit values and upper limit values of the film thickness. For example, the range may be 10  $\mu\text{m}$  or more and 1,000  $\mu\text{m}$  or less, 20  $\mu\text{m}$  or more and 500  $\mu\text{m}$  or less, or 50  $\mu\text{m}$  or more and 300  $\mu\text{m}$  or less. The film thickness of the metal plating can be measured, for example, by using a digital micrometer to measure the thickness of the resin base material before the metal plating is applied and the thickness of the resin-metal composite body after the metal plating is applied, and calculating the difference by subtracting the thickness of the resin base material before metal plating from the thickness of the resin-metal composite body after metal plating.

**[0057]** The metal plating having a structure in which a plurality of layers are laminated is not particularly limited and can be appropriately selected according to a purpose. However, it is preferable to use a stretchable metal material as an underlayer and a rigid metal material as an upper layer. For example, by forming layers in the order of a copper plating layer, which has stretchability, and a nickel plating layer, which has rigidity, it is possible to improve both the adhesion during deformation under stress and the mechanical properties.

**[0058]** In this case, the thickness of the stretchable metal plating layer is preferably 1 time or more, and more preferably 1.5 times, with respect to the thickness of the rigid metal plating layer, and particularly preferably 2 times or more and 5 times or less, from the viewpoint of compatibility of following properties between the stretchable metal plating layer and the rigid metal plating layer.

#### (Method of Manufacturing Resin-Metal Composite Body)

**[0059]** Embodiments of the present invention provide a method of manufacturing the above-described metal-resin composite body. Such a manufacturing method includes subjecting a resin base material having a surface roughness  $S_q$  of 1.5  $\mu\text{m}$  or more and a surface roughness  $S_{ku}$  of 4.5  $\mu\text{m}$  or less to a plating treatment.

**[0060]** The method of manufacturing the resin-metal composite body preferably does not include a step of subjecting the resin base material to a surface treatment such as an acid treatment and a blast treatment.

**[0061]** In the plating treatment, a method known in the art can be used, in accordance with the metal used for plating. For example, in the case of nickel plating, electroless plating can be used, and in the case of copper plating, electrolytic plating can be used. Further, to form a metal plating having a structure in which a plurality of layers are laminated, a combination of a plurality of plating methods can be used to form a metal plating in which a plurality of layers are laminated. When

electrolytic plating is used, it is desirable to form an electrically conductive layer (underlayer), because it is not possible to subject the resin base material directly to electrolytic plating. Therefore, in one embodiment, the plating treatment includes an underlayer formation step in which electroless plating is used, and then, an electrolytic plating layer formation step in which electrolytic plating is used. For example, a nickel plating may be formed first as an underlayer by electroless plating, and then, a copper plating may be formed by electrolytic plating. In the electrolytic plating layer formation step, a plurality of electrolytic plating processes using different metals may be performed. For example, an electrolytic copper plating process may be followed by an electrolytic nickel plating process. In a preferred embodiment, to apply a rigid nickel plating on a stretchable copper plating, it is preferable to perform an electroless plating step (underlayer formation), followed by an electrolytic copper plating step (copper plating formation), and further, followed by an electroless or electrolytic nickel plating step (nickel plating formation). Moreover, instead of the nickel plating formation or after the nickel plating formation, an electroless chromium plating step may be performed.

**[0062]** An example of an underlayer formation step in which the electroless plating process is used typically includes an electroless nickel plating process, which can be performed by the following method, for example.

**[0063]** First, the resin base material is immersed in a 200 mL container containing a 2 mol NaOH aqueous solution and washed by ultrasonic cleaning for 15 minutes, and then, washed by using pure water.

**[0064]** Subsequently, the resin base material is dried in a thermostatic chamber at 60°C for 20 minutes, and then, immersed in a NICKEL BOOMER CON1 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 24°C for 10 minutes, and then, washed with pure water.

**[0065]** Next, the resin base material is immersed in a NICKEL BOOMER 46 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 1 minute, and then, washed with pure water.

**[0066]** Afterwards, the resin base material is immersed in a NICKEL BOOMER 8509B-B solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 30 seconds, and then, washed with pure water.

**[0067]** Subsequently, the steps after the immersion in the NICKEL BOOMER 46 solution are repeated twice.

**[0068]** The electroless nickel plating solution is stirred with a stirrer at 60°C, washed with pure water, and dried in a thermostatic chamber at 60°C for 20 minutes.

**[0069]** Examples of the electrolytic plating formation step typically include an electrolytic copper plating process and an electrolytic nickel plating process. For example, the following method may be used in the electrolytic plating process.

**[0070]** First, the resin base material that is obtained by electroless plating in the underlayer formation step is immersed in a bath containing an electrolytic copper plating solution, to perform an electrolytic copper plating treatment by using a DC stabilized power supply IPS-3610D (manufactured by ISO-TECH) at 24°C with a current density adjusted to 4.5 A/dm<sup>2</sup>. Afterwards, the obtained product is washed with pure water.

**[0071]** After the electrolytic copper plating treatment, the resin base material is immersed in a bath containing an electrolytic nickel plating solution, to perform a nickel plating treatment by using a DC stabilized power supply IPS-3610D (manufactured by ISO-TECH) at 55°C with a current density adjusted to 5 A/dm<sup>2</sup>. Afterwards, the obtained product is washed with pure water.

**[0072]** In one aspect, the method further includes an electroless plating formation step after the electrolytic plating formation step. Typically, an electroless nickel plating process and an electroless chromium plating process are used in the electroless plating formation step. For example, the following method may be used in the electroless plating formation step.

**[0073]** First, the resin base material obtained by electrolytic plating in the second step is immersed in a 200 mL container containing a 2 mol NaOH aqueous solution and washed by ultrasonic cleaning for 15 minutes, and then, washed by using pure water.

**[0074]** Subsequently, the resin base material is dried in a thermostatic chamber at 60°C for 20 minutes, and then, immersed in a NICKEL BOOMER CON1 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 24°C for 10 minutes, and then, washed with pure water.

**[0075]** Next, the resin base material is immersed in a NICKEL BOOMER 46 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 1 minute, and then, washed with pure water.

**[0076]** Afterwards, the resin base material is immersed in a NICKEL BOOMER 8509B-B solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 30 seconds, and then, washed with pure water.

**[0077]** Subsequently, the steps after the immersion in the NICKEL BOOMER 46 solution are repeated twice.

**[0078]** Afterwards, the electroless nickel plating solution is stirred with a stirrer at 60°C, and then, washed with pure water and dried in a thermostatic chamber at 60°C for 20 minutes.

**[0079]** In the electroless plating formation step, it is preferable to use an electroless nickel solution containing a phosphorus-nickel compound having a phosphorus content of 5% or more to perform the electroless nickel plating process. This makes it possible to improve the acid resistance, the abrasion resistance, the ductility, and the like.



[Examples]

**[0080]** Embodiments of the present invention will be described in more detail below with reference to examples, but the present invention is not limited to the examples described below.

**[0081]** In the following examples, the term "parts" refers to "parts by mass" and "%" refers to "mass%".

<Preparation of Ink>

**[0082]** Based on the materials and the content (parts by mass) illustrated in Table 1 below, ultraviolet-curable compositions 1 to 23 (may be referred to as "inks 1 to 23" hereinafter) were prepared by a typical method.

Table 1

Ink No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Monomer	DCP	65	70	68	60	70	55	65	65	65	65	65	65	65	65	63	60	70	65	70	70	50	70
	VISCOAT #200						10																
	HEA							5															
Oligomer	CN104												25										25
	EBECRYL 8606	25	25	25	25	25	25	25	25	25	25	25		25	25	25	25	25	25	25	25	25	
Butadiene-containing acrylate																						20	
Filler	CELLENPIA	5	0.5	2	10	0.1	5	0.1					5	5	5	5	5						
	SENAF P210							5															
	SS 05C-413								5														
	BMI-TMH									5													
	SC-5500										5												
	PBT											5											
	AHP-200															2	5		5				
Cross-linking agent	KBM-503													0.5		0.5	0.5			0.5			
	KBM-603														0.5						0.5	0.5	
Pigment dispersion	Pig A	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Polymerization initiator	TPO	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Total		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

**[0083]** The product names and names of manufacturing companies of the materials of the inks listed in Table 1 are mentioned below.

[Monomer]

**[0084]**

- DCP: Tricyclodecane dimethanol diacrylate (manufactured by Shin-Nakamura Chemical Co., Ltd.)
- HEA: Hydroxyethyl acrylate (manufactured by Osaka Organic Chemical Industry Ltd.)
- VISCOAT #200: Cyclic trimethylolpropane formal acrylate (manufactured by Osaka Organic Chemical Industry Ltd.)

[Oligomer]

**[0085]**

- CN104 (manufactured by Sartomer Corporation)
- EBECRYL 8606 (manufactured by Daicel Corporation)

[Filler]

**[0086]**

- CELLENPIA (manufactured by Nippon Paper Industries Co., Ltd.)
- SENAF (manufactured by Hattori Shoten Co., Ltd.)

- SS05-413 (manufactured by Nitto Boseki Co., Ltd.)
- BMI-TMH (manufactured by Daiwa Kasei Industrial Co., Ltd.)
- SC-5500 (manufactured by Admatechs Co., Ltd.)
- PBT (manufactured by Ricoh Co., Ltd.)

[Cross-Linking Agent]

**[0087]**

- KBM-503 (manufactured by Shin-Etsu Chemical Co., Ltd.)
- KBM-603 (manufactured by Shin-Etsu Chemical Co., Ltd.)

[Polymerization Initiator]

**[0088]** TPO: 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (manufactured by BASF)

[Pigment]

**[0089]**

- Pigment obtained by mixing a polymer dispersant S32000 (manufactured by Lubrizol Japan Ltd.) in a mass ratio of 3:1 with Carbon Black #10 (manufactured by Mitsubishi Chemical Group Corporation)

(Examples 1 to 10 and Comparative Examples 1 to 5)

<Preparation of Resin Base Material>

**[0090]** The inks illustrated in Tables 2 and 3 below were used to fill a 3D printer (MARS 3 Pro, manufactured by ELEGOO) and a molded object having a size of 4.0 x 1.0 x 80.0 mm was created under conditions including a resolution of 4098 x 2560, a layer height of 0.05 mm, a number of initial layers of 5, an exposure time of the initial layer of 35 seconds, and an exposure time of 2.5 seconds. A secondary curing device (Form Cure, manufactured by Formlabs) was used to perform secondary curing at 60°C for 90 minutes to form a resin base material.

<Surface Treatment>

**[0091]** The surface of the formed resin base material was subjected to the surface treatments (blast treatments 1 to 10 and acid treatment 1) listed in Table 3 below. The surface roughness Sq and the surface roughness Sku were measured by the method described below.

**[0092]** The measurement results are illustrated in Tables 2 and 3.

<Method of Measuring Surface Roughness Sq and Surface Roughness Sku>

**[0093]** The surface roughness Sq and the surface roughness Sku of the formed resin base material (resin base material after surface treatment) were measured in an Opt-SEM measurement in high image quality depth synthesis mode by using an electron microscope (Keyence Corporation VHX7000) at a magnification of 1500 times to obtain an image of the surface of the resin base material and calculate the surface roughness by using the analysis software of the electron microscope.

**[0094]** The details of the processes in the blast treatments 1 to 10 and the acid treatment 1 are described below.

- Blast Treatment 1 -

**[0095]** Each side of the formed resin base material was subjected to a blast treatment using a SHAVE MEDIA Y-80 (manufactured by Fuji Manufacturing Co., Ltd.) and a sandblaster having a diameter of 1.5 cm, under conditions including an injection pressure of the medium of 0.2 MPa, a distance between the nozzle of the sandblaster and the laminated body of 1 cm, and an injection time of the medium of 1 second. A medium adhering to the obtained sample after treatment was removed by using an air gun at an injection pressure of 0.2 MPa.

- Blast Treatment 2 -

**[0096]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 0.3 MPa.

- Blast Treatment 3 -

**[0097]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 0.4 MPa.

- Blast Treatment 4 -

**[0098]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 0.5 MPa.

- Blast Treatment 5 -

**[0099]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 0.6 MPa.

- Blast Treatment 6 -

**[0100]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 1 MPa.

- Blast Treatment 7 -

**[0101]** A treatment similar to blast treatment 3 was performed, except that the distance between the nozzle of the sandblaster and the laminated body in blast treatment 3 was changed from 1 cm to 10 cm.

- Blast Treatment 8 -

**[0102]** A treatment similar to blast treatment 3 was performed, except that the distance between the nozzle of the sandblaster and the laminated body in blast treatment 3 was changed from 1 cm to 20 cm.

- Blast Treatment 9 -

**[0103]** A treatment similar to blast treatment 3 was performed, except that the distance between the nozzle of the sandblaster and the laminated body in blast treatment 3 was changed from 1 cm to 30 cm.

- Blast Treatment 10 -

**[0104]** A treatment similar to blast treatment 1 was performed, except that the injection time of the medium in blast treatment 1 was changed from 1 second to 20 seconds.

- Blast Treatment 11 -

**[0105]** A treatment similar to blast treatment 1 was performed, except that the injection time of the medium in blast treatment 1 was changed from 1 second to 30 seconds.

- Blast Treatment 12 -

**[0106]** A treatment similar to blast treatment 1 was performed, except that the injection pressure in blast treatment 1 was changed from 0.2 MPa to 0.1 MPa.

- Acid Treatment 1 -

**[0107]** The formed resin base material was immersed in a 200 mL container containing a 2 mol NaOH aqueous solution,

washed by ultrasonic cleaning for 15 minutes, and then, washed by using pure water. Afterwards, the resin base material was dried in a thermostatic chamber at 60°C for 20 minutes.

**[0108]** Subsequently, 400 g/dm<sup>3</sup> of chromic anhydride (manufactured by Kanto Kagaku Co., Ltd.) and 400 g/dm<sup>3</sup> of sulfuric acid (manufactured by Kanto Kagaku Co., Ltd.) were added to pure water to prepare an aqueous chromic acid solution, and the resin base material was immersed in the prepared aqueous chromic acid solution and stirred by using a stirrer at 70°C for 5 minutes.

**[0109]** Next, the resin base material was washed with pure water and dried in a thermostatic chamber at 60°C for 20 minutes.

<Metal Plating Treatment (may be referred to as "Metal Plating Treatment 1" hereinafter)>

- First Step (Electroless Plating) -

**[0110]** The formed resin base material (the resin base material after the surface treatment) was immersed in a 200 mL container containing a 2 mol NaOH aqueous solution, washed by ultrasonic cleaning for 15 minutes, and then, washed by using pure water.

**[0111]** Subsequently, the resin base material was dried in a thermostatic chamber at 60°C for 20 minutes, and then, immersed in a NICKEL BOOMER CON1 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 24°C for 10 minutes, and then, washed with pure water.

**[0112]** Next, the resin base material was immersed in a NICKEL BOOMER 46 solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 1 minute, and then, washed with pure water.

**[0113]** Afterwards, the resin base material was immersed in a NICKEL BOOMER 8509B-B solution (manufactured by Nihon Kagaku Sangyo Co., Ltd.), stirred with a stirrer at 60°C for 30 seconds, and then, washed with pure water.

**[0114]** Subsequently, the steps after the immersion in the NICKEL BOOMER 46 solution were repeated twice.

**[0115]** Thereafter, an electroless nickel plating solution 1 (NICKEL BOOMER 8509M, manufactured by Nihon Kagaku Sangyo Co., Ltd.) was stirred with a stirrer at 60°C, and then, washed with pure water and dried in a thermostatic chamber at 60°C for 20 minutes.

- Second Step (Electrolytic Plating) -

**[0116]** The resin base material obtained by electroless plating in the first step was immersed in a bath containing an electrolytic copper plating solution obtained in the preparation example described below, to perform the electrolytic copper plating treatment by using a DC stabilized power supply IPS-3610D (manufactured by ISO-TECH) at 24°C with a current density adjusted to 5 A/dm<sup>2</sup>. Afterwards, the obtained product was washed with pure water.

**[0117]** The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1 μm was formed and on the nickel plating layer, a copper plating layer having a film thickness of 5 μm was formed.

-- Example of Preparing Electrolytic Copper Plating Solution --

**[0118]** The electrolytic copper plating solution was obtained by adding 200 g/L of copper sulfate pentahydrate (manufactured by Kanto Kagaku Co., Ltd.), 0.15 g/L of copper chloride dihydrate (manufactured by Kanto Kagaku Co., Ltd.), and 50 g/L of sulfuric acid (manufactured by Kanto Kagaku Co., Ltd.) to pure water and adjusting the pH to 0.5.

**[0119]** In Examples 1 to 10 and Comparative Examples 1 to 5, the adhesion between the resin base material and the metal plating (may be referred to as "adhesion" hereinafter) was evaluated. The evaluation results are listed in Tables 2 and 3.

(Adhesion)

**[0120]** A cutter guide was used to cut the resin-metal composite body 11 times lengthwise and crosswise at 1 mm intervals, to create a grid pattern of 100 squares. A piece of CELLOTAPE (registered trademark) No. 405 manufactured by Nichiban was firmly pressed onto the grid pattern and peeled off quickly to check the frequency of exposed squares of the base material, and evaluate the adhesion between the resin base material and the metal plating, based on the following evaluation criteria.

[Evaluation Criteria]

**[0121]**

# EP 4 484 608 A1

A: Peeling occurs in less than 20% of the total squares

B: Peeling occurs in 20% or more and less than 50% of the total squares

C: Peeling occurs in 50% or more of the total squares

Table 2

		Examples							
		1	2	3	4	5	6	7	8
	Ink No.	18	18	18	18	18	18	18	18
	Blast treatment No.	1	2	3	4	5	7	8	10
	Acid treatment No.	-	-	-	-	-	-	-	-
Metal plating	Metal plating treatment No.	1	1	1	1	1	1	1	1
	First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
	Second layer Film thickness (μm)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)
Surface roughness	Sq	2.55	3.07	3.42	1.73	2.41	2.25	1.87	2
	Sku	2.46	2.64	2.39	4.13	2.98	2.88	3.02	2.84
Evaluation results	Adhesion	B	A	A	A	B	A	B	B

Table 3

		Examples		Comparative Examples				
		9	10	1	2	3	4	5
	Ink No.	1	22	18	18	18	18	18
	Blast treatment No.	3	-	6	9	11	12	-
	Acid treatment No.	-	1	-	-	-	-	1
Metal plating	Metal plating treatment No.	1	1	1	1	1	1	1
	First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
	Second layer Film thickness (μm)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)
Surface roughness	Sq	2.4	3.31	1.41	1.45	1.2	1.94	1.85
	Sku	2.54	2.45	4.33	4.61	4.37	6.21	4.72
Evaluation results	Adhesion	A	A	C	C	C	C	C

## EP 4 484 608 A1

(Examples 11 to 27 and Comparative Examples 6 to 11)

### <Preparation of Resin Base Material>

- 5 **[0122]** Resin base materials were formed by a method similar to the one in Example 1, using the inks listed in Tables 4 to 6 below. The surface roughness Sq and the surface roughness Sku were measured by a method similar to the one in Example 1. The measurement results are listed in Tables 4 to 6.

### <Metal Plating Treatment>

- 10 **[0123]** The formed resin base material was subjected to a metal plating treatment using a method similar to the one in Example 1, to form a resin-metal composite body.

- 15 **[0124]** In Examples 11 to 27 and Comparative Examples 6 to 11, the adhesion between the resin base material and the metal plating was evaluated by a method similar to the one in Example 1. The evaluation results are listed in Tables 4 to 6.

Table 4

		Examples							
		11	12	13	14	15	16	17	18
20	Ink No.	1	2	3	4	5	6	7	8
	Blast treatment No.	-	-	-	-	-	-	-	-
	Acid treatment No.	-	-	-	-	-	-	-	-
25	Metal plating	Metal plating treatment No.	1	1	1	1	1	1	1
30		First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
35		Second layer Film thickness (μm)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)
40	Surface roughness	Sq	1.57	1.61	1.63	1.66	1.52	1.7	1.55
		Sku	3.71	4	3.68	3.28	4.2	3.24	4.12
	Evaluation results	Adhesion	A	A	A	A	B	A	A

Table 5

		Examples							
		19	20	21	22	23	24	25	26
45	Ink No.	9	10	11	12	13	14	15	16
50	Blast treatment No.	-	-	-	-	-	-	-	-
	Acid treatment No.	-	-	-	-	-	-	-	-

55

(continued)

		Examples							
		19	20	21	22	23	24	25	26
Metal plat- ing	Metal plating treatment No.	1	1	1	1	1	1	1	1
	First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
	Second layer Film thickness (μm)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)
Surface roughness	Sq	10.09	3.86	2.55	2.66	1.74	4.17	3.8	2.43
	Sku	4.08	2.39	2.86	3.44	3.91	3.06	3.23	3.12
Evaluation results	Adhesion	A	A	B	B	A	A	A	A

Table 6

		Example	Comparative Examples					
		27	6	7	8	9	10	11
Ink No.		17	18	19	20	21	22	23
Blast treatment No.		-	-	-	-	-	-	-
Acid treatment No.		-	-	-	-	-	-	-
Metal plating	Metal plating treatment No.	1	1	1	1	1	1	1
	First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
	Second layer Film thickness (μm)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)	Copper (5)
Surface roughness	Sq	2.71	1.88	1.24	1.22	1.31	1.53	1.4
	Sku	2.58	5.76	6.65	3.81	4.1	4.72	4.93
Evaluation results	Adhesion	A	C	C	C	C	C	C

(Examples 28 to 56 and Comparative Examples 12 to 14)

## &lt;Preparation of Resin Base Material&gt;

**[0125]** Resin base materials were formed by a method similar to the one in Example 1, using the inks listed in Tables 7 to 10 below.

## &lt;Surface Treatment&gt;

**[0126]** The surface of the formed resin base material was subjected to the surface treatments listed in Tables 7 to 10. The surface roughness Sq and the surface roughness Sku were measured by a method similar to the one in Example 1. The

measurement results are listed in Tables 7 to 10.

#### <Metal Plating Treatment>

**[0127]** The formed resin base material (the resin base material after surface treatment, in a case where a surface treatment is performed) was subjected to metal plating treatments (metal plating treatments 1 to 16) listed in Tables 7 to 10. The details of the processes in the metal plating treatments 2 to 16 are described below.

#### - Metal Plating Treatment 2 -

**[0128]** A metal plating treatment was performed similarly to the metal plating treatment 1, except that, in the metal plating treatment 1, in the first step, the immersion time in the electroless nickel plating solution 1 was changed to 200 minutes and the second step was not performed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 10  $\mu\text{m}$  was formed.

#### - Metal Plating Treatment 3 -

**[0129]** A metal plating treatment was performed similarly to the metal plating treatment 1, except that, in the metal plating treatment 1, the treatment time in the electrolytic copper plating treatment was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, and on the electroless nickel plating layer, a copper plating layer having a film thickness of 5  $\mu\text{m}$  was formed.

#### - Metal Plating Treatment 4 -

**[0130]** A metal plating treatment was performed similarly to the metal plating treatment 1, except that, in the metal plating treatment 1, the electrolytic copper plating solution was changed to the electrolytic nickel plating solution obtained in the preparation example described below, and an electrolytic nickel plating treatment was performed according to a procedure described below. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, and on the electroless nickel plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed.

#### -- Preparation Example of Electrolytic Nickel Plating Solution 3 --

**[0131]** The electrolytic nickel plating solution was obtained by adding 300 g/L of nickel sulfate hexahydrate (manufactured by Kanto Kagaku Co., Ltd.), 45 g/L of nickel chloride hexahydrate (manufactured by Fujifilm Wako Pure Chemical Industries, Ltd.), and 40 mg/L of boric acid to pure water and adjusting the pH to a value of 2.5 to 5.

#### -- Electrolytic Nickel Plating --

**[0132]** The resin base material obtained by electroless plating in the first step was immersed in a bath containing an electrolytic nickel plating solution, to perform a nickel plating treatment by using a DC stabilized power supply IPS-3610D (manufactured by ISO-TECH) at 55°C with a current density adjusted to 5 A/dm<sup>2</sup>. Afterwards, the obtained product was washed with pure water.

#### - Metal Plating Treatment 5 -

**[0133]** A metal plating treatment was performed similarly to the metal plating treatment 1, except that, in the second step of the metal plating treatment 1, an electrolytic nickel plating solution was further used to perform an electrolytic nickel plating treatment and the treatment time in the copper plating treatment was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 10  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed.

#### - Metal Plating Treatment 6 -

**[0134]** A metal plating treatment was performed similarly to the metal plating treatment 5, except that, in the metal plating treatment 5, the treatment time in the copper plating treatment and the treatment time in the nickel plating treatment were



changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 20  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 10  $\mu\text{m}$  was formed.

- Metal Plating Treatment 7 -

**[0135]** A metal plating treatment was performed similarly to the metal plating treatment 6, except that the treatment time in the nickel plating treatment in the metal plating treatment 6 was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 20  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed.

- Metal Plating Treatment 8 -

**[0136]** A metal plating treatment was performed similarly to the metal plating treatment 7, except that the treatment time in the copper plating treatment in the metal plating treatment 7 was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 30  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed.

- Metal Plating Treatment 9 -

**[0137]** A metal plating treatment was performed similarly to the metal plating treatment 7, except that the treatment time in the copper plating treatment in the metal plating treatment 7 was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 100  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed.

- Metal Plating Treatment 10 -

**[0138]** A metal plating treatment was performed similarly to the metal plating treatment 5, except that the treatment time in the nickel plating treatment in the metal plating treatment 5 was changed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 10  $\mu\text{m}$  was formed, and on the copper plating layer, a nickel plating layer having a film thickness of 10  $\mu\text{m}$  was formed.

- Metal Plating Treatment 11 -

**[0139]** A metal plating treatment was performed similarly to the metal plating treatment 8, except that, in the second step of the metal plating treatment 8, an electrolytic chromium plating solution obtained in the preparation example described below was further used to perform an electrolytic chromium plating treatment according to a procedure described below. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 30  $\mu\text{m}$  was formed, on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed, and on the nickel plating layer, a chromium plating layer having a film thickness of 0.5  $\mu\text{m}$  was formed.

-- Example of Preparing Electrolytic Chromium Plating Solution --

**[0140]** The above-mentioned electrolytic chromium plating solution was obtained by adding 250 g/L of chromic anhydride (manufactured by Kanto Kagaku Co., Ltd.) and 2.5 g/L of sulfuric acid (manufactured by Kanto Kagaku Co., Ltd.) to pure water and adjusting the pH to a value of 0.5 to 4.

-- Electrolytic Chromium Plating --

**[0141]** The resin base material was immersed in a bath containing an electrolytic chromium plating solution, to perform a chromium plating treatment by using a DC stabilized power supply IPS-3610D (manufactured by ISO-TECH) at 55°C with a current density adjusted to 10 A/dm<sup>2</sup>. Afterwards, the obtained product was washed with pure water.

## - Metal Plating Treatment 12 -

**[0142]** A metal plating treatment was performed similarly to the metal plating treatment 8, except that, after the second step in the metal plating treatment 8, a third step described below was further performed. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 30  $\mu\text{m}$  was formed, on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed, and on the nickel plating layer, a nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed.

## - Third Step (Electroless Plating) -

**[0143]** The resin base material after the electroless plating treatment in the second step was immersed in a 200 mL container containing a 1 mol NaOH aqueous solution and washed by ultrasonic cleaning for 15 minutes, and then, washed by using pure water.

**[0144]** Subsequently, the resin base material was dried in a thermostatic chamber at 60°C for 20 minutes, and then, immersed in the NICKEL BOOMER CON1 solution, stirred with a stirrer at 24°C for 10 minutes, and then, washed with pure water.

**[0145]** Next, the resin base material was immersed in the NICKEL BOOMER 46 solution, stirred with a stirrer at 60°C for 1 minute, and then, washed with pure water.

**[0146]** Afterwards, the resin base material was immersed in the NICKEL BOOMER 8509B-B solution, stirred with a stirrer at 60°C for 30 seconds, and then, washed with pure water.

**[0147]** Subsequently, the steps after the immersion in the NICKEL BOOMER 46 solution were repeated twice.

**[0148]** An electroless nickel plating solution obtained in the preparation example described below was stirred with a stirrer at 60°C, and then, washed with pure water and dried in a thermostatic chamber at 60°C for 20 minutes.

## -- Preparation Example of Electroless Nickel Plating Solution 3 --

**[0149]** The electroless nickel plating solution 3 was obtained by adding 16 g/L of nickel sulfate (manufactured by Kanto Kagaku Co., Ltd.), 24 g/L of sodium phosphinate (manufactured by Kanto Kagaku Co., Ltd.), 16 g/L of sodium succinate (manufactured by Fuji Film Wako Pure Chemical Industries, Ltd.), and 18 g/L of malic acid (manufactured by Fuji Film Wako Pure Chemical Industries, Ltd.) to pure water and adjusting the pH to 5.6.

## - Metal Plating Treatment 13 -

**[0150]** A metal plating treatment was performed similarly to the metal plating treatment 2, except that the electroless nickel plating solution 1 in the metal plating treatment 2 was changed to an electroless nickel plating solution 2 obtained in the preparation example described below. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 10  $\mu\text{m}$  was formed.

## -- Preparation Example of Electroless Nickel Plating Solution 2 --

**[0151]** The electroless nickel plating solution 2 was obtained by adding 30 g/L of nickel sulfate (manufactured by Kanto Kagaku Co., Ltd.), 10 g/L of sodium phosphinate (manufactured by Kanto Kagaku Co., Ltd.), and 10 g/L of sodium acetate (manufactured by Fujifilm Wako Pure Chemical Industries, Ltd.) to pure water and adjusting the pH to a value of 4 to 6.

## - Metal Plating Treatment 14 -

**[0152]** A metal plating treatment was performed similarly to the metal plating treatment 8, except that the electroless nickel plating solution 1 in the metal plating treatment 8 was changed to the electroless nickel plating solution 2. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 30  $\mu\text{m}$  was formed, on the copper plating layer, a nickel plating layer having a film thickness of 20  $\mu\text{m}$  was formed, and on the nickel plating layer, a nickel plating layer having a film thickness of 1  $\mu\text{m}$  was formed.

## - Metal Plating Treatment 15 -

**[0153]** A metal plating treatment was performed similarly to the metal plating treatment 2, except that the electroless nickel plating solution 1 in the metal plating treatment 2 was changed to an electroless copper plating solution obtained in

the preparation example described below. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless copper plating layer having a film thickness of 10 μm was formed.

-- Example of Preparing Electroless Copper Plating Solution --

**[0154]** The electroless copper plating solution was prepared by adding 7 g/L of copper sulfate pentahydrate (manufactured by Kanto Kagaku Co., Ltd.), 25 g/L of EDTA (manufactured by Sigma-Aldrich Corporation), 6.5 mL/L of 40% formaldehyde (manufactured by Fuji Film Wako Pure Chemical Industries, Ltd.), and 60 mg/L of sodium cyanide (manufactured by Fuji Film Wako Pure Chemical Industries, Ltd.) to pure water and adjusting the pH to 12.6.

- Metal Plating Treatment 16 -

**[0155]** A metal plating treatment was performed similarly to the metal plating treatment 8, except that the electroless nickel plating solution 1 in the metal plating treatment 8 was changed to the electroless copper plating solution. The layer structure and the film thickness of the metal plating were measured, and it was found that an electroless nickel plating layer having a film thickness of 1 μm was formed, on the electroless nickel plating layer, a copper plating layer having a film thickness of 30 μm was formed, on the copper plating layer, a nickel plating layer having a film thickness of 20 μm was formed, and on the nickel plating layer, a nickel plating layer having a film thickness of 1 μm was formed.

**[0156]** In Examples 28 to 56 and Comparative Examples 12 to 14, the "three-point bending stress", the "adhesion after a three-point bending stress test", the "corrosion resistance", and the "reproducibility" were evaluated based on the following evaluation criteria.

**[0157]** The evaluation results are listed in Tables 7 to 10.

(Three-Point Bending Stress)

**[0158]** The resin-metal composite body was subjected to a three-point bending test in conformity with JIS K7171 by using an autograph AGS-X (manufactured by Shimadzu Corporation), to measure the three-point bending stress. The three-point bending stress was evaluated from the measurement results, based on the following evaluation criteria. The three-point bending stress was calculated from the maximum test force (bending load) using the following mathematical expressions.

$$\text{bending stress } \sigma = \frac{3FL}{2bh^2}, \text{ bending strain } \epsilon = \frac{600sh}{L^2}$$

F: bending load, L: distance between supporting points, b: width of test piece, h: thickness of test piece, s: deflection

[Evaluation Criteria]

**[0159]**

- S: Three-point bending stress of 80 N/mm<sup>2</sup> or more
- A: Three-point bending stress of 60 N/mm<sup>2</sup> or more and less than 80 N/mm<sup>2</sup>
- B: Three-point bending stress of 40 N/mm<sup>2</sup> or more and less than 60 N/mm<sup>2</sup>
- C: Three-point bending stress of less than 40 N/mm<sup>2</sup>

(Adhesion after Three-Point Bending Test)

**[0160]** After the three-point bending test, the adhered state between the resin base material and the metal plating of the resin-metal composite body was visually observed, and the adhesion after the three-point bending test was evaluated, based on the following evaluation criteria.

[Evaluation Criteria]

**[0161]**

- A: Shape does not change
- B: Metal plating peels off from resin base material, and surface has localized roughness and waviness

## EP 4 484 608 A1

C: Metal plating completely peels off from resin base material, and surface has strong roughness and waviness

(Corrosion Resistance)

**[0162]** The resin-metal composite body was sprayed with 5% neutral salt water so that the adhesion amount was  $20 \pm 5$  mg/cm<sup>2</sup>, and was left to stand at 35°C for 1 hour. Afterwards, the change of the shape was visually observed, and the corrosion resistance was evaluated based on the following evaluation criteria.

[Evaluation Criteria]

**[0163]**

A: Shape does not change

B: Localized discoloration is observed

C: Discoloration is observed in entire sample

(Reproducibility)

**[0164]** The resin-metal composite body was cut three times lengthwise and crosswise at 5 mm intervals, to create a grid pattern. A piece of CELLOTAPE (registered trademark) No. 405 manufactured by Nichiban was firmly pressed onto the grid pattern and peeled off quickly to check the frequency of exposed parts of the base material, and the evaluation of the adhesion between the resin base material and the metal plating was repeated three times, based on the evaluation criteria of the adhesion described below. The reproducibility was evaluated from the results of the three evaluations of the adhesion, based on the following evaluation criteria of the reproducibility.

[Evaluation Criteria of Adhesion]

**[0165]**

A: Peeling occurs in less than 20% of the entire surface

B: Peeling occurs in 20% or more and less than 50% of the entire surface

C: Peeling occurs in 50% or more of the entire surface

[Evaluation Criteria of Reproducibility]

**[0166]**

3: 3 evaluation results of "B" or better among 3 evaluations of adhesion

2: 2 or more and less than 3 evaluation results of "B" or better among 3 evaluations of adhesion

1: 1 or more and less than 2 evaluation results of "B" or better among 3 evaluations of adhesion

0: 0 evaluation results of "B" or better among 3 evaluations of adhesion

Table 7

	Examples								
	28	29	30	31	32	33	34	35	36
Ink No.	1	1	1	1	1	1	1	1	1
Blast treatment No.	-	-	-	-	-	-	-	-	-
Acid treatment No.	-	-	-	-	-	-	-	-	-

**EP 4 484 608 A1**

(continued)

			Examples								
			28	29	30	31	32	33	34	35	36
5	Metal plating	Metal plating treatment No.	1	2	3	4	5	6	7	8	9
		First layer Film thickness (μm)	Nickel (1)	Nickel (10)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
10		Second layer Film thickness (μm)	Copper (5)	-	Copper (20)	Nickel (20)	Copper (10)	Copper (20)	Copper (20)	Copper (30)	Copper (100)
		Third layer Film thickness (μm)	-	-	-	-	Nickel (20)	Nickel (10)	Nickel (20)	Nickel (20)	Nickel (20)
15		Fourth layer Film thickness (μm)	-	-	-	-	-	-	-	-	-
20	Surface roughness	Sq	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57	1.57
		Sku	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71	3.71
25	Evaluation results	Three-point bending stress	C	C	B	A	A	B	A	A	A
		Adhesion after three-point bending test	A	A	A	C	C	A	B	A	A
		Corrosion resistance	A	C	C	B	B	B	B	B	B
30		Reproducibility	3	3	3	3	3	3	3	3	3

Table 8

35			Examples							
			37	38	39	40	41	42	43	44
	Ink No.		1	1	1	1	1	1	1	18
	Blast treatment No.		-	-	-	-	-	-	-	3
40	Acid treatment No.		-	-	-	-	-	-	-	-
45	Metal plating	Metal plating treatment No.	10	11	12	13	14	15	16	11
		First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (10)	Nickel (1)	Copper (10)	Copper (1)	Nickel (1)
		Second layer Film thickness (μm)	Copper (10)	Copper (30)	Copper (30)		Copper (30)		Copper (30)	Copper (30)
		Third layer Film thickness (μm)	Nickel (10)	Nickel (20)	Nickel (20)		Nickel (20)		Nickel (20)	Nickel (20)
		Fourth layer Film thickness (μm)		Chromium (0.5)	Nickel (1)					Chromium (0.5)
55	Surface roughness	Sq	1.57	1.57	1.57	1.57	1.57	1.57	1.57	3.42
		Sku	3.71	3.71	3.71	3.71	3.71	3.71	3.71	2.39

**EP 4 484 608 A1**

(continued)

		Examples							
		37	38	39	40	41	42	43	44
Evaluation results	Three-point bending stress	B	A	A	C	A	C	A	A
	Adhesion after three-point bending test	B	A	A	C	A	C	A	A
	Corrosion resistance	B	A	A	B	B	C	B	A
	Reproducibility	3	3	3	3	3	3	3	1

Table 9

		Examples						
		45	46	47	48	49	50	51
Ink No.		18	22	22	8	8	9	9
Blast treatment No.		3	-	-	-	-	-	-
Acid treatment No.		-	1	1	-	-	-	-
Metal plating	Metal plating treatment No.	12	11	12	11	12	11	12
	First layer Film thickness (μm)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)
	Second layer Film thickness (μm)	Copper (30)	Copper (30)	Copper (30)	Copper (30)	Copper (30)	Copper (30)	Copper (30)
	Third layer Film thickness (μm)	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (20)
	Fourth layer Film thickness (μm)	Nickel (1)	Chromium (0.5)	Nickel (1)	Chromium (0.5)	Nickel (1)	Chromium (0.5)	Nickel (1)
Surface roughness	Sq	3.42	3.31	3.31	1.67	1.67	10.09	10.09
	Sku	2.39	2.45	2.45	3.17	3.17	4.08	4.08
Evaluation results	Three-point bending stress	A	A	A	A	A	A	A
	Adhesion after three-point bending test	A	A	A	A	A	A	A
	Corrosion resistance	A	A	A	A	A	A	A
	Reproducibility	1	1	1	3	3	3	3

Table 10

		Examples					Comparative Examples		
		52	53	54	55	56	12	13	14
Ink No.		10	10	17	17	1	1	18	22

(continued)

5			Examples					Comparative Examples		
			52	53	54	55	56	12	13	14
	Blast treatment No.		-	-	-	-	-	-	-	-
	Acid treatment No.		-	-	-	-	-	-	-	-
10	Metal plating	Metal plating treatment No.	11	12	11	12	17	-	-	-
		First layer Film thickness ( $\mu\text{m}$ )	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	Nickel (1)	-	-	-
15		Second layer Film thickness ( $\mu\text{m}$ )	Copper (30)	Copper (30)	Copper (30)	Copper (30)	Copper (90)	-	-	-
		Third layer Film thickness ( $\mu\text{m}$ )	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (20)	Nickel (60)	-	-	-
20		Fourth layer Film thickness ( $\mu\text{m}$ )	Chromium (0.5)	Nickel (1)	Chromium (0.5)	Nickel (1)	Nickel (1)	-	-	-
25	Surface roughness	Sq	3.86	3.86	2.71	2.71	1.57	1.57	1.88	1.53
		Sku	2.39	2.39	2.58	2.58	3.71	3.71	5.76	4.72
30	Evaluation results	Three-point bending stress	A	A	A	A	S	C	B	C
		Adhesion after three-point bending test	A	A	A	A	A	C	B	C
		Corrosion resistance	A	A	A	A	A	A	A	A
35		Reproducibility	3	3	3	3	3	0	0	0

**[0167]** Aspects of the present invention include the following, for example.

**[0168]** According to a first aspect, a resin-metal composite body includes a resin base material having a surface roughness Sq of 1.5  $\mu\text{m}$  or more and a surface roughness Sku of 4.5  $\mu\text{m}$  or less, and a metal plating on the resin base material.

**[0169]** According to a second aspect, in the resin-metal composite body according to the first aspect, the resin base material includes a filler.

**[0170]** According to a third aspect, in the resin-metal composite body according to the second aspect, the filler includes at least one of a cellulose nanofiber, a glass fiber, and a bismaleimide resin.

**[0171]** According to a fourth aspect, in the resin-metal composite body according to any one of the first to third aspects, the metal plating has an average film thickness of 20  $\mu\text{m}$  or more.

**[0172]** According to a fifth aspect, in the resin-metal composite body according to any one of the first to fourth aspects, the metal plating includes at least one of a copper plating and a nickel plating.

**[0173]** According to a sixth aspect, in the resin-metal composite body according to any one of the first to fifth aspects, the metal plating includes a copper plating and a nickel plating, and a thickness of the copper plating is one time or more with respect to a thickness of the nickel plating.

**[0174]** According to a seventh aspect, in the resin-metal composite body according to any one of the first to sixth aspects, the resin base material has neither an acid treatment nor a blast treatment.

**[0175]** According to an eighth aspect, a method of manufacturing a resin-metal composite body includes subjecting a resin base material having a surface roughness Sq of 1.5  $\mu\text{m}$  or more and a surface roughness Sku of 4.5  $\mu\text{m}$  or less to a plating treatment.

**[0176]** According to a ninth aspect, in the method according to the eighth aspect, the plating treatment includes forming an underlayer by electroless plating, and forming an electrolytic plating layer by electrolytic plating.

**[0177]** According to a tenth aspect, in the method according to the ninth aspect, the plating treatment further includes forming an electroless plating layer, after the forming the electrolytic plating layer, by using an electroless nickel solution including a phosphorus-nickel compound having a phosphorus content of 5% or more.

**[0178]** According to an eleventh aspect, the method according to any one of the eighth to tenth aspects does not include subjecting the resin base material to an acid treatment or a blast treatment.

**[0179]** Any one of the above-described operations may be performed in various other ways, for example, in an order different from the one described above.

## Claims

1. A resin-metal composite body (100), comprising:

a resin base material (10) having a surface roughness Sq of 1.5  $\mu\text{m}$  or more and a surface roughness Sku of 4.5  $\mu\text{m}$  or less; and  
a metal plating (20) on the resin base material (10).

2. The resin-metal composite body (100) according to claim 1, wherein the resin base material (10) includes a filler.

3. The resin-metal composite body (100) according to claim 2, wherein the filler includes at least one of a cellulose nanofiber, a glass fiber, and a bismaleimide resin.

4. The resin-metal composite body (100) according to any one of claims 1 to 3, wherein the metal plating (20) has an average film thickness of 20  $\mu\text{m}$  or more.

5. The resin-metal composite body (100) according to any one of claims 1 to 4, wherein the metal plating (20) includes at least one of a copper plating and a nickel plating.

6. The resin-metal composite body (100) according to any one of claims 1 to 5, wherein the metal plating (20) includes a copper plating and a nickel plating, and a thickness of the copper plating is one time or more with respect to a thickness of the nickel plating.

7. The resin-metal composite body (100) according to any one of claims 1 to 6, wherein the resin base material (10) has neither an acid treatment nor a blast treatment.

8. A method of manufacturing a resin-metal composite body, the method comprising:  
subjecting a resin base material having a surface roughness Sq of 1.5  $\mu\text{m}$  or more and a surface roughness Sku of 4.5  $\mu\text{m}$  or less to a plating treatment.

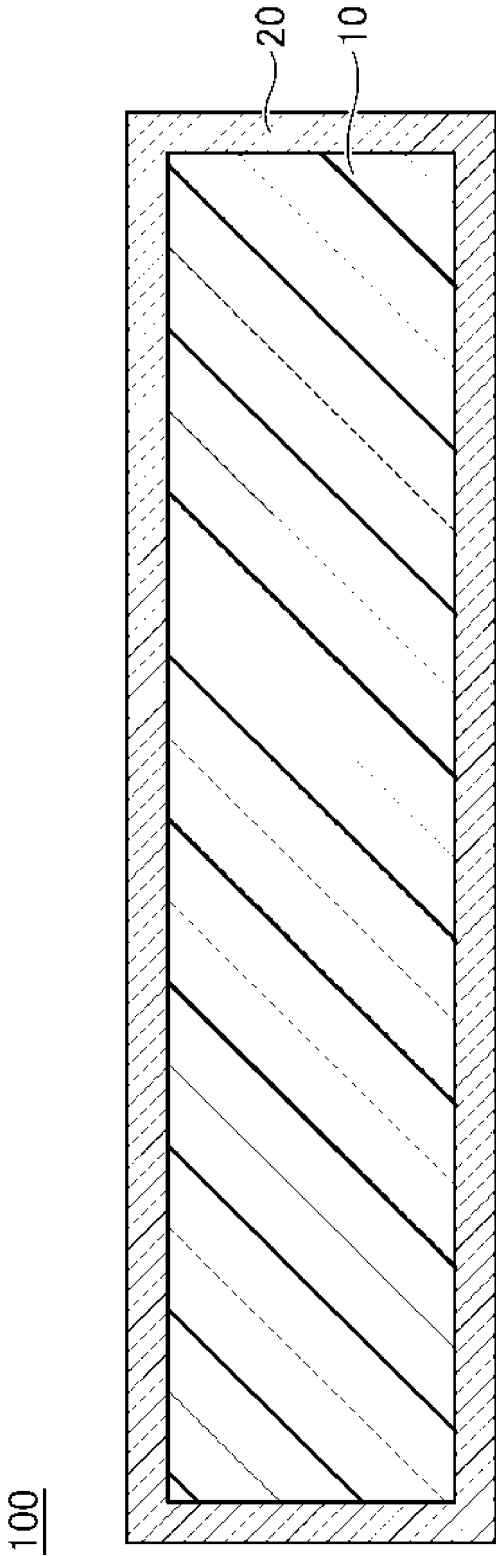
9. The method according to claim 8, wherein the plating treatment includes:

forming an underlayer by electroless plating; and  
forming an electrolytic plating layer by electrolytic plating.

10. The method according to claim 9, wherein the plating treatment further includes:  
forming an electroless plating layer, after the forming the electrolytic plating layer, by using an electroless nickel solution including a phosphorus-nickel compound having a phosphorus content of 5% or more.

11. The method according to any one of claims 8 to 10, wherein the method does not include subjecting the resin base material to an acid treatment or a blast treatment.







## EUROPEAN SEARCH REPORT

Application Number

EP 24 18 3271

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	Chen Meixin ET AL: "Surface Preparation of Polymeric Substrates for Cold Spraying Coatings", , 1 September 2021 (2021-09-01), pages 1-137, XP093197984, Retrieved from the Internet: URL:https://www.proquest.com/docview/2700377762?pq-origsite=gscholar&fromopenview=true&sourcetype=Dissertations%20&%20Theses [retrieved on 2024-08-19]	1-4,7,8,11	INV. C23C18/36 C23C18/16
Y	* section 3.1; page 28 * * section 3.2; page 33 * * section 3.3; page 36 * * page 59; figure 4.19 * * page 63; figure 4.24 * * page 68; figure 4.29 * * page 66; table 4.2 *	5,6,9,10	TECHNICAL FIELDS SEARCHED (IPC)
Y	CN 113 564 593 A (SHENZHEN SUNWAY COMMUNICATION CO LTD) 29 October 2021 (2021-10-29) * claim 1 * * paragraphs [0044], [0046], [0052] *	5,6,9,10	C23C
The present search report has been drawn up for all claims			
Place of search <b>The Hague</b>		Date of completion of the search <b>17 September 2024</b>	Examiner <b>Lampert, Felix</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 24 18 3271

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17 - 09 - 2024

10	Patent document cited in search report	Publication date	Patent family member(s)	Publication date
15	CN 113564593	A	29 - 10 - 2021	NONE
20				
25				
30				
35				
40				
45				
50				
55				

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- JP 2008290295 A [0002]