

Two Layered Gold Plating Method and Electronic Component

Technical Field

[0001]

- 5 The present invention relates to a new gold plating method for preventing corrosion of an underlying metal and to an electronic component produced by the method.

Background Art

10 [0002]

Gold, superior in physical and mechanical properties, has a high conductive property next to silver and copper in addition to a high ductility and high corrosion resistance, thereby gold is used for a wiring material and a contact material in the field of electronic industry.

A hard gold plating is applied as a finish surface treatment on a high reliable contact material such as a connector and a compact relay. The thickness of such a gold plated layer is required to be 3 μ m or above for obtaining good corrosion resistance. If the thickness is less than 3 μ m, there remains a pinhole and good corrosion resistance is not achieved. The above is strictly required for a contact material and is a common knowledge in the industry. Namely, the pinhole of a plated layer increases in an exponential fashion and corrosion resistance is remarkably deteriorated when the thickness is reduced.

[0003]

Patent Literature 1 proposes a sealing treatment of a pinhole

of an electric contact point with a noble metal plating using a sealing treatment liquid as a technology for eliminating a pinhole produced on a plated layer.

Patent Literature 1 discloses a sealing treatment method of a pinhole of a plated material wherein an underlying metal is plated with gold, silver, rhodium, palladium, ruthenium, or alloy thereof and the plated material is D.C. electrolyzed in an aqueous solution. The aqueous solution includes an organic compound having a corrosion inhibition effect for one underlying metal or more than one underlying metals, pH of the aqueous solution being larger than 7.0, the anode current density being $0.3\text{A}/\text{dm}^2$ or above, and the current amount being $0.15\text{ coulomb}/\text{dm}^2$ or above.

15 [0004]

When a contact material is plated, durability for repeating open-close operations of the contact point is required in addition to small contact resistance.

In view of abrasion resistance of the contact material, Patent Literature 2 proposes a technology of plating gold or gold-cobalt alloy on a nickel plated base. Patent Literature 3 proposes a technology of improving corrosion resistance of a gold plated product wherein a metal product is applied with nickel plating and a gold plating is further applied thereon. Patent Literature 4 proposes that a tinned layer is formed on phosphor bronze and a liquid lubricant with specific composition is applied.

Patent Literature 3 discloses one example of the prior art for

improving corrosion resistance of a gold plated product.

Patent Literature 3 relates to a sealing treatment method of a pinhole of a plated material with gold or gold-alloy having an underlying layer plated with nickel or alloy including nickel.

5 D.C. electrolysis is applied using the plated material as an anode from 0.1V to 5.0V of voltage E between electrodes in an emulsion type sealing treatment liquid produced by adding self-emulsifier in 0.01 to 5.0 weight percent in an inhibitor aqueous liquid. The object of Patent Literature 3 is to provide
10 a gold plated material, contact point, with no environmental contamination, low contact resistance and high corrosion resistance.

Citation List

15 Patent Literature

[0005]

PTL 1 : Japanese unexamined Patent Publication H05-311492

PTL 2 : Japanese unexamined Patent Publication H02-173288

PTL 3 : Japanese unexamined Patent Publication H09-170096

20 PTL 4 : Japanese examined Patent Publication H05-22322

Summary of Invention

Technical Problem

[0006]

25 The above-mentioned Patent Literature 3 requires application of a nickel plating or an alloy plating including nickel as a base layer on an underlying metal, thereby complicating an operation procedure and requiring troublesome works.

Nickel plating is applied as a base layer and a gold plating is further applied thereon, so that the contact resistance becomes higher than that of a single gold plating. Therefore, such a plating is not desirable for an electronic component such as a contact point which requires remarkably low contact resistance.

[0007]

In case of a gold plating on a contact point of a relay, the thickness of a plated layer is required to be 3 μ m or above in view of corrosion resistance as mentioned above.

However, gold is an expensive precious metal, so that it is required to reduce the consumption amount of gold by reducing the thickness of the gold-plated layer. Such a reduction has been highly requested recently because of rising gold price. In response to such a request, the present invention proposes a gold plating method with superior corrosion resistance at low cost and an electronic component for a contact point produced by the gold plating method.

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Solution to Problem

[0008]

As a result of earnest investigation, the inventor of the present invention has achieved the method of the present invention with a simple operation procedure, remarkably low gold consumption, and enough corrosion resistance.

In the two layered gold plating method of the present invention, the method comprises the steps of forming a base gold-plated

layer on a surface of a metal to be plated as a first plating, and forming a finish gold-plated layer as a second plating by an electrolytic method depositing a gold crystal smaller than that of the base gold-plated layer on a surface of the base gold-plated layer.

The first plating of the base gold-plated layer is not limited to a prior gold plating method by an electrolytic method and includes a gold plating by an electroless method or a gold plating by vapor deposition. The finish gold-plated layer formed by the second plating is applied by an electrolytic method like the prior gold plating method, so that a specific plating apparatus is not required.

[0009]

In the finish plating liquid used for the second plating treatment of the present invention, soluble gold salt or gold complex is dissolved in an aqueous liquid including at least aliphatic amine of 3 to 8 weight percent and organic acid of 3 to 8 weight percent.

Soluble gold salt and gold complex include gold(I) potassium cyanide, gold(II) potassium cyanide, ammonium dicyanoaurate, gold(I) potassium chloride, gold(II) potassium chloride, gold(I) sodium chloride, gold(II) sodium chloride, gold potassium thiosulfate, gold sodium thiosulfate, gold potassium sulfite, gold sodium sulfite, and so on. In the present invention the combination thereof can be used.

[0010]

The finish plating liquid used in the second plating is developed by the inventor of the present invention as a result of earnest investigation, wherein soluble gold salt or gold complex is dissolved in a base aqueous liquid including aliphatic amine and organic acid such as citric acid for neutralizing aliphatic amine by a predetermined ratio. However, soluble gold salt or gold complex can be mixed later in the base solution prepared in advance.

10 The finish plating liquid is able to be used as electrolysis solution in the second plating process executing an electrolytic method. In such a case, minute gold crystal is deposited compared with the gold plated layer formed by the prior electrolytic method, so that a plated film grows at slow speed.

15 As a result, a pinhole remaining on the base gold-plated layer is effectively sealed. In addition, the finish gold-plated layer covers the base gold-plated layer after sealing the pinhole, so that the finish layer is integrated with the base layer with no difference in appearance, color and gloss.

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[0011]

In the second aspect of the present invention, an electronic component has a gold plated layer formed by the two layered gold plating method of the present invention.

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Advantageous Effects of Invention

[0012]

In the present invention, the pinhole is sealed by minute gold

crystal particles at the time of forming the finish gold-plated layer even when the pinhole remains on the base gold-plated layer. Therefore, when the entire gold plated layer of the base gold-plated layer and the finish gold-plated layer is thin, the consumption amount of expensive gold is remarkably reduced, achieving the same anticorrosion property as that of prior art.

[0013]

In the prior gold plating method, the thickness of gold plated layer is required to be $3\mu\text{m}$ in order to obtain practical corrosion resistance. However, in the experiment by the inventor of the present invention, the same corrosion resistance is achieved even when the thickness of the base gold-plated layer is $2\mu\text{m}$ or below and that of the finish gold-plated layer is $0.8\mu\text{m}$ or below.

Brief Description of Drawings

[0014]

Fig.1a and Fig.1b show diagrammatical sectional views of a material applied with a base gold plating and a material applied with a finish gold plating, respectively.

Fig.2a and Fig.2b show examples of microscope photographs of the surfaces of the base gold-plated layer and the finish gold-plated layer, respectively.

Fig.3 is a flow chart showing basic procedures of a two layered gold plating method of the present invention.

Fig.4 shows a basic structure of a plating apparatus for the finish gold plating.

Description of Embodiments

[0015]

The present invention proposes a two layered gold plating method wherein a base gold plating is applied in general conditions
5 as the first plating treatment and then a finish gold plating is applied as the second plating treatment.

[0016]

A pure-gold plated layer or a hard gold plated layer is formed
10 as the base gold-plated layer by a general electrolytic method. The practical conditions, such as composition of a plating liquid, voltage and current between the anode and the cathode, treatment temperature, and treatment time, are empirically determined in view of cost and quality.

15 The method is not limited to an electrolytic method and a gold plating by an electroless method or a gold plating by vapor deposition can be applied on the base gold-plated layer.

[0017]

20 When a gold plating is applied for a metal product constituting a contact point of an electronic component such as a relay device, corrosion resistance of a gold plated portion is especially important in order to keep enough durability of the electronic component.

25 Gold has very low ionization tendency, so that the plated layer does not corrode. However, when a pinhole remains on the plated layer, the underlying metal portion directly under the pinhole is exposed to outer air and corrosive gas and sometimes corrodes.

The corrosion of the underlying metal portion is accelerated by the gold plated layer, which is contrary to galvanization, and such a problem should not be disregarded.

5 [0018]

Generally in an electrolytic method, the anode, the cathode and a material to be plated are immersed in a plating liquid in which metal salt forming a plated layer is dissolved. D.C., voltage is applied between the anode and the cathode while the material
10 to be plated contacts the cathode, metal ion in the plating liquid is reduced and deposited on the surface of the material to be plated, and metal crystal is produced. A plurality of deposited metal crystals are grown and integrated, a layer is formed on the entire surface of the material to be plated, and the entire
15 surface is plated with the layer.

In response to the reduction reaction at the cathode, the anode shows oxidation reaction, thus current flows between the anode and the cathode. In the plating treatment, products other than a plated layer are generated and the kinds of the products depend
20 on the composition and pH value of the plating liquid.

[0019]

In such an electrolytic method, small crystals firstly deposited on the surface of the material to be plated grow as a core and
25 are integrated, thereby forming a plated layer. Therefore, the layer has a convexo-concave surface on a microscopic level and a pinhole is sometimes caused on the concave portion where the plated layer is thin. A small portion of the plated layer which

does not attach the base layer remains as a pinhole. A crack caused when the materials to be plated physically contact with each other sometimes becomes a pinhole.

5 [0020]

Conventionally, the gold plating applied on the contact point of an electronic component generally requires thickness of at least $3\mu\text{m}$ in order that corrosion caused by the pinhole does not become a practical problem. However, the thickness of $3\mu\text{m}$
10 is not small in the field of a gold plating and a considerable amount of gold is consumed, thereby increasing the cost.

[0021]

In the present invention, a base gold-plated layer is formed
15 on the surface of the material to be plated such as a contact point of an electronic component. Then, the material to be plated with a base gold-plated layer is immersed in the above-mentioned finish plating liquid and the finish gold-plated layer is further formed by an electrolytic method.
20 Therefore, the finish gold plating is applied in the same manner as the prior gold plating method by the electrolytic method, thereby facilitating application of the above.

[0022]

25 The electrolytic solution used as the finish gold plating liquid is composed such that soluble metal salt or gold complex is dissolved in an aqueous liquid including at least aliphatic amine of 3 to 8 weight percent and organic acid of 3 to 8 weight percent.

Aliphatic amine includes condensed amine and organic acid includes citric acid, acetic acid, or oxalic acid. Soluble gold salt or gold complex includes gold(I) potassium cyanide, gold(II) potassium cyanide, ammonium dicyanoaurate, gold(I) potassium chloride, gold(II) potassium chloride, gold(I) sodium chloride, gold(II) sodium chloride, gold potassium thiosulfate, gold sodium thiosulfate, gold potassium sulfite, gold sodium sulfite, and so on. In the present invention the combination thereof can be used.

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[0023]

About 70g to 150g of gold cyanide is mixed in a solution of 10 liters and a pH adjuster and a brightening agent are used if necessary.

15 The pH adjuster includes an aqueous solution of sulfate amino compound and the brightening agent includes an aqueous solution including chloroplatinic acid.

A desirable pH value is from pH4 to pH6.

20 [0024]

In the finish plating treatment, it is preferable that voltage of 4V to 6V is applied between the anode and the cathode to flow current of 0.7A to 1.5A. The treatment time depends on the thickness required for the finish gold-plated layer.

25

[0025]

When a gold plating is applied by the electrolytic method using the above-mentioned finish plating liquid as an electrolytic

solution, growth of the plated layer becomes slow compared with a general plating method of the electrolytic method. However, an elaborate plated layer is obtained by depositing minute crystals. Therefore, even when the thickness of the base gold-plated layer is reduced and a pinhole remains, the pinhole is sealed by the minute crystal particle deposited when the finish gold-plated layer is formed, thereby reducing gold consumption.

10 [0026]

In the finish gold plating, after the pinhole remaining on the base gold-plated layer is sealed, the crystal particles are shaped so as to form a thin layer on the surface of the base gold-plated layer. In view of gold consumption and treatment time, the base gold-plated layer may be $1.2\mu\text{m}$ or below in thickness and the finish gold-plated layer may be $0.8\mu\text{m}$ or below in thickness. Such values are determined in view of enough margin, but the gold consumption becomes $2/3$ of the prior gold plated layer of $3\mu\text{m}$ thickness.

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[0027]

Under strict control, it is desirable that the base gold-plated layer is $0.9\mu\text{m}$ or below in thickness and the finish gold-plated layer is $0.6\mu\text{m}$ or below in thickness. In such a case, the gold consumption becomes $1/3$ of the prior gold plated layer of $3\mu\text{m}$ thickness.

[0028]

The two layered plating method of the present invention is explained referring to the attached drawings.

5 [0029]

Fig.1a shows a diagrammatical sectional view of a material applied with the base gold plating and Fig.1b shows a diagrammatical sectional view of a material applied with the finish gold plating on the base gold-plated layer.

10

[0030]

In Fig.1a, a material to be plated 1 is, for example, steel and a base gold-plated layer 2 is formed on the surface of the material as the first plating treatment. The base gold-plated layer 2 has a concavo-convex surface and a pinhole is generated by a minute no-attachment portion 3 and a crack 4.

[0031]

When a finish gold-plated layer 5 is formed on the upper surface of the base gold-plated layer 2 as the second plating treatment, the finish gold-plated layer 5 covers the base gold-plated layer 2 and the pinholes 3, 4. Thus the pinholes are completely sealed by the finish gold-plated layer 5.

25 [0032]

It is confirmed by an experiment that the base gold-plated layer 2 and the finish gold-plated layer 5 are integrated in such a manner that they are not distinguished in appearance.

[0033]

Fig.2a and Fig.2b show examples of microscope photographs of the surfaces of the base gold-plated layer and the finish gold-plated layer, respectively.

- 5 The base gold-plated layer 2 has a rough concavo-convex surface, on the other hand, the finish gold-plated layer 5 has a very smooth surface.

[0034]

- 10 The basic procedures of the two layered gold plating method of the present invention are explained referring to the drawings.

[0035]

- 15 Fig.3 is a flow chart showing the basic procedures. The conditions are different in the base gold plating and in the finish gold plating, so that separate equipment is required for the finish gold plating in addition to the equipment for the base gold plating.

20 [0036]

- The step 100 in the flow chart is a procedure of the base gold plating wherein the material to be plated is inserted in the base gold plating equipment. After the step 100, the material formed with the base gold-plated layer is taken out of the
25 equipment and is cleaned in the step 101.

In the step 102, the cleaned material is inserted in the finish gold plating equipment for executing the finish gold plating. After the step 102, the material formed with the finish

gold-plated layer is taken out of the equipment and is cleaned in the step 103.

In the step 104, a sample is extracted for quality test from the materials formed with the finish gold-plated layer. The corrosion resistance, the hardness of the plated layer and so on are checked in the quality test.

[0037]

The finish gold plating equipment is explained referring to the drawings.

[0038]

Fig.4 shows a slant-barrel-type plating apparatus for the finish gold plating. The material to be plated is a contact point member for an electronic component.

[0039]

A barrel 11 of a plating equipment 10 is made of resin with insulation property. The upper part of the barrel 11 is open, the central axis is slant and the barrel is driven to be rotated by a motor 12. The vertically sectional view of the barrel 11 is shown in the figure for illustrating the internal structure. An anode 13 is inserted from an opening 11a of the barrel 11 and a cathode 14 is provided on the bottom of the barrel 11. The barrel 11 includes finish plating liquid 20 the amount of which does not overflow from the opening 11a and includes one batch of metal products 30 in the finish plating liquid 20. While the barrel 11 is rotated, current is applied between the anode

13 and the cathode 14, thereby forming a film of the plated finish layer on the entire surface of the metal product 1.

Reference Signs List

- 5 [0040]
 - 1 material to be plated
 - 2 base gold-plated layer
 - 3, 4 pinhole
 - 5 finish gold-plated layer
- 10 13 anode
- 14 cathode

Claims

1. A two layered gold plating method comprising the steps of :
forming a base gold-plated layer equal to or less than $1.2\mu\text{m}$
5 in thickness in which range of less than $0.9\mu\text{m}$ is excluded on
a surface of a metal to be plated as a first plating; and
forming a finish gold-plated layer being equal to or less than
 $0.8\mu\text{m}$ in thickness as a second plating by an electrolytic method
depositing a gold crystal smaller than that of said base
10 gold-plated layer on a surface of said base gold-plated layer.
2. The two layered gold plating method as set forth in claim
1, said finish gold-plated layer is formed with a finish plating
liquid in which soluble gold salt or gold complex is dissolved
15 in an aqueous liquid including at least aliphatic amine of 3
to 8 weight percent and organic acid of 3 to 8 weight percent.
3. An electronic component comprising a contact material of which
metal to be plated has a gold plated layer formed by a two layered
20 gold plating method,
wherein a base gold-plated layer equal to or less than $1.2\mu\text{m}$
in thickness in which range of less than $0.9\mu\text{m}$ is excluded is
formed on a surface of said metal to be plated, and
wherein a finish gold-plated layer being equal to or less than
25 $0.8\mu\text{m}$ in thickness formed by an electrolytic method depositing
a gold crystal smaller than that of said base gold-plated layer
is formed on a surface of said base gold-plated layer.