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(54) SILVER-PLATED MATERIAL AND METHOD FOR MANUFACTURING SAME

(57) There is provided a silver-plated product having a more excellent wear resistance than that of conventional silver-plated products while maintaining the high hardness thereof, and a method for producing the same. In a method for producing a silver-plated product by forming a surface layer of silver on a base material by electroplating in a silver-plating solution which is an aqueous solution containing silver potassium cyanide, potassium cyanide and a mercaptothiazole, the concentration of the mercaptothiazole in the silver-plating solution is not lower than 5 g/L, and the electroplating is carried out at a liquid temperature of not lower than 30 °C and at a current density of 1 to 15 A/cm^2.

Processed by Luminess, 75001 PARIS (FR)

Description

Technical Field

[0001] The present invention generally relates to a silver-plated product and a method for producing the same. More specifically, the invention relates to a silver-plated product used as the material of contact and terminal parts, such as connectors, switches and relays, which are used for on-vehicle and/or household electric wiring, and a method for producing the same.

Background Art

[0002] As conventional materials of contact and terminal parts, such as connectors and switches, there are used plated products wherein a base material of copper, a copper alloy, stainless steel or the like, which are relatively inexpensive and which have excellent corrosion resistance, mechanical characteristics and so forth, is plated with tin, silver, gold or the like in accordance with required characteristics, such as electrical and soldering characteristics.

[0003] Tin-plated products obtained by plating a base material of copper, a copper alloy, stainless steel or the like, with tin are inexpensive, but they do not have good corrosion resistance in a high-temperature environment. Gold-plated products obtained by plating such a base material with gold have excellent corrosion resistance and high reliability, but the costs thereof are high. On the other hand, silver-plated products obtained by plating such a base material with silver are inexpensive in comparison with gold-plated products and have excellent corrosion resistance in comparison with tin-plated products.

[0004] The materials of contact and terminal parts, such as connectors and switches, are also required to have good wear resistance against the insertion and extraction of connectors and/or the sliding movements of switches.

[0005] However, silver-plated products are soft and easy to wear. For that reason, if the silver-plated product is used as the material of a connecting terminal or the like, there is a problem in that the insertion and extraction and/or the sliding movement cause the adhesion thereof to easily cause the adhesive abrasion thereof. There is also a problem in that the surface of the connecting terminal is shaved to enhance the coefficient of friction thereof to enhance the insertion force thereof when the connecting terminal is inserted.

[0006] In order to solve such problems, there is known a method for improving the hardness of the silver-plated product by causing the silver-plating film thereof to contain an element, such as antimony (see, e.g., Patent Document 1).

Prior Art Document(s)

Patent Document(s)

[0007] Patent Document 1: JP 2009-79250 A (Paragraph Numbers 0003-0004)

Summary of the Invention

Problem to be solved by the Invention

[0008] However, if the silver-plating film is caused to contain an element, such as antimony, as the method of Patent Document 1, the improvement of the wear resistance is not sufficient although silver is alloyed to improve the hardness thereof. For that reason, it is desired to provide a silver-plated product having a more excellent wear resistance.

[0009] It is therefore an object of the present invention to eliminate the aforementioned conventional problems and to provide a silver-plated product having a more excellent wear resistance than that of conventional silver-plated products while maintaining the high hardness thereof, and a method for producing the same.

Means for solving the Problem

[0010] In order to accomplish the aforementioned object, the inventors have diligently studied and found that it is possible to provide a silver-plated product having a more excellent wear resistance than that of conventional silver-plated products while maintaining the high hardness thereof, and a method for producing the same, if the silver-plated product is produced by a method for forming a surface layer of silver on a base material by electroplating at a liquid temperature of not lower than 30 °C and at a current density of 1 to 15 A/cm^2 in a silver-plating solution which is an aqueous solution containing silver potassium cyanide, potassium cyanide and a mercaptothiazole wherein the concentration of the mercaptothiazole in the silver-plating solution is not lower than 5 g/L. Thus, the inventors have made the present invention.

[0011] According to the present invention, there is provided a method for producing a silver-plated product, the method comprising the steps of: preparing a silver-plating solution which is an aqueous solution containing silver potassium cyanide, potassium cyanide and a mercaptothiazole; and forming a surface layer of silver on a base material by electroplating at a liquid temperature of not lower than 30 °C and at a current density of 1 to 15 A/cm^2 in the silver-plating solution, wherein the concentration of the mercaptothiazole in the silver-plating solution is not lower than 5 g/L.

[0012] In this method for producing a silver-plated product, the concentration of the mercaptothiazole in the silver-plating solution is preferably not lower than 10 g/L. The concentration of the mercaptothiazole in the silver-plating solution is preferably not higher than 30 g/L, and more preferably not higher than 25 g/L. The current density in the electroplating is preferably in the range of from 2 A/cm^2 to 10 A/cm^2. The concentration of the silver potassium cyanide in the silver-plating solution is preferably in the range of from 50 g/L to 200 g/L, and the concentration of the potassium cyanide in the silver-plating solution is preferably in the range of from 20 g/L to 120 g/L. The concentration of silver in the silver-plating solution is preferably in the range of from 20 g/L to 120 g/L, and the concentration of free cyanide in the silver-plating solution is preferably in the range of from 5 g/L to 50 g/L. The electroplating is preferably carried out at a liquid temperature of not higher than 50 °C. The base material is preferably made of copper or a copper alloy, and an underlying layer of nickel is preferably formed between the base material and the surface layer.

[0013] According to the present invention, there is provided a silver-plated product comprising: a base material; and a surface layer of silver which is formed on the base material, the surface layer having an average crystallite size of not greater than 23 nm and having a Vickers hardness HV of 100 to 160, the surface layer containing not less than 0.3 % by weight of carbon, not less than 0.4 % by weight of sulfur and not less than 0.1 % by weight of nitrogen.

[0014] In this silver-plated product, the surface layer preferably contains 90 to 99 % by weight of silver. The surface layer preferably contains not higher than 2 % by weight of carbon, and preferably contains not higher than 2 % by weight of sulfur. The base material is preferably made of copper or a copper alloy, and an underlying layer of nickel is preferably formed between the base material and the surface layer.

Effects of the Invention

[0015] According to the present invention, it is possible to provide a silver-plated product having a more excellent wear resistance than that of conventional silver-plated products while maintaining the high hardness thereof, and a method for producing the same.

Mode for Carrying Out the Invention

[0016] In the preferred embodiment of a method for producing a silver-plated product according to the present invention, a surface layer of silver is formed on a base material by electroplating at a liquid temperature of not lower than 30 °C and at a current density of 1 to 15 A/cm^2 in a silver-plating solution which is an aqueous solution containing silver potassium cyanide, potassium cyanide and a mercaptothiazole wherein the concentration of the mercaptothiazole in the silver-plating solution is not lower than 5 g/L.

[0017] If a mercaptothiazole is thus added to a silver-plating solution as an organic addition agent, it is considered that it is possible to incorporate the mercaptothiazole into a silver-plating film (a surface layer of silver) by electroplating to suppress the movement of transformation in the silver-plating film to enhance the hardness of the silver-plated product to improve the wear resistance thereof while decreasing the coefficient of friction of the silver-plated product by the lubricating effect of the organic addition agent. In particular, the mercaptothiazole has a dithioimino carbonate structure to easily dissociate protons thereof to have a high solubility in an aqueous solution to be easily incorporated into the silver-plating film, so that it is possible to improve the deposition rate of the silver-plating film. In addition, even if the deposition rage is high, it is possible to improve the abrasion resistance thereof unlike N-allylthiourea and 2-mercaptobenzimidazole.

[0018] In this method for producing a silver-plated product, the concentration of the mercaptothiazole in the silver-plating solution is preferably not lower than 10 g/L and preferably not higher than 30 g/L (more preferably not higher than 25 g/L) . The electroplating for forming the silver-plating layer is preferably carried out at a current density of 2 to 10 A/dm^2. The concentration of silver potassium cyanide in the silver-plating solution is preferably 50 to 200 g/L and more preferably 70 to 180 g/L. The concentration of potassium cyanide in the silver-plating solution is preferably 20 to 120 g/L and more preferably 30 to 100 g/L. The concentration of silver in the silver-plating solution is preferably 20 to 120 g/L, more preferably 30 to 110 g/L and most preferably 40 to 100 g/L. The concentration of free cyanide in the silver-plating solution is preferably 5 to 50 g/L, more preferably 10 to 45 g/L and most preferably 15 to 40 g/L. The electroplating for forming the silver-plating layer is preferably carried out at a liquid temperature of not higher than 50 °C , more preferably carried out at a liquid temperature of not higher than 45 °C, and most preferably carried out at a liquid temperature of not higher than 40 °C, The base material is preferably made of copper or a copper alloy. Between the base material and the surface layer, an underlying layer of nickel is preferably formed. This underlying layer of nickel can be formed by electroplating in a publicly-known nickel-plating bath (preferably a sulfamic acid bath), such as a Watts bath or a sulfamic acid bath.

[0019] The preferred embodiment of a silver-plated product according to the present invention comprises: a base material; and a surface layer of silver which is formed on the base material, the surface layer having an average crystallite size of not greater than 23 nm and having a Vickers hardness HV of 100 to 160, the surface layer containing not less than 0.3 % by weight of carbon, not less than 0.4 % by weight of sulfur and not less than 0.1 % by weight of nitrogen.

[0020] In this silver-plated product, the content of silver in the surface layer is preferably 90 to 99 % by weight, more preferably 92 to 99 % by weight, and most preferably 95 to 99 % by weight. The content of carbon in the surface layer is preferably not lower than 0.5 % by weight, and preferably not higher than 2 % by weight (more preferably not higher than 1 % by weight). The content of sulfur in the surface layer is preferably not lower than 0.6 % by weight and preferably not higher than 2 % by weight (more preferably not higher than 1.5 % by weight). The content of nitrogen in the surface layer is preferably not lower than 0.2 % by weight and preferably not higher than 2 % by weight (more preferably not higher than 1 % by weight and most preferably not higher than 0.5 % by weight). The content of potassium in the surface layer is preferably 0.1 to 2 % by weight and more preferably 0.2 to 1 % by weight. The ratio (C/S) of the content (atomic concentration at%) of carbon to the content (atomic concentration at%) of sulfur in the surface layer is preferably 1.5 to 2.5. The ratio (SIN) of the content (atomic concentration at%) of sulfur to the content (atomic concentration at%") of nitrogen in the surface layer is preferably 1.0 to 2.5. The ratio (C/N) of the content (atomic concentration at%) of carbon to the content (atomic concentration at%) of nitrogen in the surface layer is preferably 2.5 to 4.0. Between the base material and the surface layer, an underlying layer of nickel is preferably formed.

Examples

[0021] Examples of a silver-plated product and a method for producing the same according to the present invention will be described below in detail.

[Example 1]

[0022] First, a rolled sheet of oxygen-free copper (C1020 1/2H) having a size of 67 mm x 50 mm x 0.3 mm was prepared as a base material (a material to be plated). As the pretreatment thereof, the material and a SUS plate were put in an alkali degreasing solution to be used as a cathode and an anode, respectively, to carry out electrolytic degreasing at 5 V for 30 seconds. The material thus electrolytic-degreased was washed with water, and then, pickled for 15 seconds in a 3% sulfuric acid to be washed with water.

[0023] Then, the material thus pretreated and a nickel electrode plate were used as a cathode and an anode, respectively, to electroplate (dull-nickel-plate) the material at a liquid temperature of 55 °C and at a current density of 5 A/dm^2 for 60 seconds in a dull-nickel-plating solution of an aqueous solution containing 540 g/L of nickel sulfamate tetrahydrate, 25 g/L of nickel chloride and 35 g/L of boric acid, while stirring the solution at 500 rpm by means of a stirrer. After a dull-nickel-plating film was thus formed as an underlying plating film, the thickness of the substantially central portion of the dull-nickel-plating film was measured by means of an X-ray fluorescent analysis thickness meter (SFT-110A produced by Hitachi High-Tech Science Corporation). As a result, the thickness was 1 μm.

[0024] Then, the material having the underlying plating film and a titanium electrode plate coated with platinum were used as a cathode and an anode, respectively, to electroplate the material at a room temperature (25 °C) and at a current density of 2.0 A/dm^2 for 10 seconds in a silver strike plating solution of an aqueous solution containing 3 g/L of silver potassium cyanide ($KAg(CN)_2$) and 90 g/L of potassium cyanide (KCN), while stirring the solution at 500 rpm by means of a stirrer. After a silver strike plating film was thus formed, it was washed with water for sufficiently washing away the silver strike plating solution.

[0025] Then, the silver-strike-plated material and a silver electrode plate were used as a cathode and an anode, respectively, to electroplate (silver-plate) the material at a liquid temperature of 35 (±0.5) °C and at a current density of 3 A/dm^2 for 200 seconds in a silver-plating solution of an aqueous solution containing 80 g/L of silver potassium cyanide ($KAg(CN)_2$), 39 g/L of potassium cyanide (KCN) and 12.4 g/L of 2-mercaptothiazole (a mercaptothiazole) (MT) (the aqueous solution containing 43.4 g/L of silver and 16 g/L of free cyanide), while stirring the solution at 500 rpm by means of a stirrer. The silver-plating film thus formed was washed with water, and then, dried with wind pressure by means of an air gun to obtain a silver-plated product.

[0026] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by means of the above-described X-ray fluorescent analysis thickness meter. As a result, the thickness was 5 μ m.

[0027] The Vickers hardness HV of this silver-plated product was measured in accordance with JIS Z2244 by applying a measuring load of 10 gf for 10 seconds using a micro-hardness testing machine (HM-221 produced by Mitutoyo Corporation). As a result, the Vickers hardness HV was 151.

[0028] Two silver-plated products, each of which was the same as the above-described silver-plated product, were prepared, one of the silver-plated products being indented (Inside R = 1.5 mm) to be used as an indenter, and the other of the silver-plated products being used as a plate-shaped evaluation sample. Then, the wear resistance of the evaluation sample was evaluated by carrying out an abrasion test for confirming the abrasion status of the evaluation sample by observing the central portion of the sliding scratch of the evaluation sample at a magnification of 100 by means of a microscope (VHX-1000 produced by Keyence Corporation) when the reciprocating sliding movement (sliding distance = 5 mm, sliding speed = 1.67 mm/s) was continued until the base material was exposed while the indenter was pushed against the evaluation sample at a constant load (5N) by means of a precision sliding testing apparatus (CRS-G2050-DWA produced by Yamasaki-Seiki Laboratory Co., Ltd.). As a result, it was confirmed that the base material was not exposed after the reciprocating sliding movement was repeated 1,000 times, so that it was found that the wear resistance thereof was good.

[0029] The crystallite sizes in vertical directions to each crystal plane of (111), (200) , (220) and (311) planes of the silver-plating film of the silver-plated product were calculated by the Scherrer's equation from the full-width at half maximum of each of peaks ((111) peak appearing at about 38°, (200) peak appearing at about 44° , (220) peak appearing at about 64° and (311) peak appearing at about 77°) on the crystal planes on an X-ray diffraction pattern (XRD pattern) obtained by means of an X-ray diffractometer (Full-Automatic Multi-Purpose Horizontal X-ray diffractometer, Smart Lab produced by RIGAKU Corporation). The calculated crystallite sizes were weighted on the basis of the orientation ratio of each of the crystal planes to calculate an average crystallite size by the weighted average of the crystallite sizes on the crystal planes. As a result, the average crystallite size of the silver-plating film was 61.0 angstroms (6.10 nm). Furthermore, as the above-described orientation ratio, there was used a value (corrected intensity) which was corrected by dividing each of the X-ray diffraction peak intensities (the intensities at X-ray diffraction peaks) on the (111), (200), (220) and (311) planes of the silver-plating film by each of the relative intensity ratios (the relative intensity ratios during the measurement of powder) described on JCPDS card No.40783 ((111) : (200); (220) : (311) = 100 : 40 : 25 : 26), the X-ray diffraction peak intensities being obtained from the X-ray diffraction pattern obtained by scanning in a scanning field $2\theta / \theta$ using a Cu tube and a Kβ filter method by means of an X-ray diffractometer (XRD) (Full-Automatic Multi-Purpose Horizontal X-ray diffractometer, Smart Lab produced by RIGAKU Corporation).

[Example 2]

[0030] A silver-plated product was produced by the same method as that in Example 1, except that the electroplating (silver-plating) for forming the silver-plating film was carried out at a current density of 5 A/dm^2 for 120 seconds.

[0031] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μm.

[0032] After silver in the silver-plated product was dissolved in nitric acid, hydrochloric acid was added thereto until the generation of a white precipitate (AgCl) was completed. Then, after the white precipitate was filtrated and washed with water, the weight of AgCl was measured to calculate the weight of silver in the silver-plating film. The content of carbon in the silver-plated product was calculated by qualitatively and quantitatively measuring CO and CO_2, which were produced when the silver-plated product was heated to 1350 °C in an oxygen gas stream to be melted, by an infrared detector by means of a carbon/sulfur analyzer (EMIA-810 produced by HORIBA, Ltd.). The content of sulfur in the silver-plated product was calculated as the content of sulfur in the silver-plating film by qualitatively and quantitatively measuring SO_2, which was produced when the silver-plated product was heated to 1350 °C in an oxygen gas stream to be melted, by the infrared detector. The content of nitrogen in the silver-plated product was calculated as the content of nitrogen in the silver-plating film by quantitatively measuring N_2, which was produced when the silver-plated product was melted in a helium gas stream by an electric power of 5000 W, by a thermal conductivity detector (TCD) by means of an oxygen/nitrogen/hydrogen analyzer (produced by LECO JAPAN CORPORATION). After the obtained silver-plated product was dissolved in nitric acid (reagent for accurate analysis), it was diluted so as to cause the concentration of potassium in this nitric acid solution not to be higher than 2 mg/L. Then, the content of potassium in the silver-plated product was measured by an atomic absorption photometer (Deflection Zeeman Atomic Absorption Photometer ZA3300 produced by Hitachi High-Tech Science Corporation). The contents of silver, carbon, sulfur, nitrogen and potassium in the silver-plated product were regarded as the contents of silver, carbon, sulfur, nitrogen and potassium in the silver-plating film, since the contents of silver, carbon, sulfur, nitrogen and potassium in the base material were not greater than detection limit although they were obtained by the same methods as the above-described methods before the silver-plating film was formed. As a result, the silver-plating film was a film containing 0.7 % by weight of carbon, 1.1 % by weight of sulfur, 0.2 % by weight of nitrogen, 0.2 % by weight of potassium and the balance being silver (Ag purity: 97.8 % by weight) assuming that the total of the contents of silver, carbon, sulfur, nitrogen and potassium was 100 % by weight. Furthermore, from the results obtained by analyzing the silver-plating film by means of the carbon/sulfur analyzer (EMIA-810 produced by HORIBA, Ltd.) and the oxygen/nitrogen/hydrogen analyzer (produced by LECO JAPAN CORPORATION), the ratios of atomic concentrations (at%) in the silver-plating film were C/S = 1.7, S/N = 2.2 and C/N = 3.8.

[0033] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 129. It was confirmed that the base material was not exposed after the reciprocating sliding movement was repeated 1,000 times, so that it was found that the wear resistance thereof was good. The average crystallite size of the silver-plating film was 148.7 angstroms (14.87 nm).

[Example 3]

[0034] A silver-plated product was produced by the same method as that in Example 1, except that a silver-plating solution of an aqueous solution containing 175 g/L of silver potassium cyanide ($KAg(CN)_2$), 95 g/L of potassium cyanide (KCN) and 18.5 g/L of 2-mercaptothiazole (a mercaptothiazole) (MT) (the aqueous solution containing 94.9 g/L of silver and 38 g/L of free cyanide) was used as the silver-plating solution and that the electroplating (silver-plating) for forming the silver-plating film was carried out at a current density of 5 A/dm^2 for 120 seconds.

[0035] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μm. The surface analysis of the silver-plating film of this silver-plated product was carried out by the same method as that in Example 2. As a result, the silver-plating film was a film containing 0.7 % by weight of carbon, 0.8 % by weight of sulfur, 0.3 % by weight of nitrogen, 0.5 % by weight of potassium and the balance being silver (Ag purity: 97.7 % by weight) (C/S = 2.2, S/N = 1.3 and C/N = 2.9).

[0036] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 129. It was confirmed that the base material was not exposed after the reciprocating sliding movement was repeated 1,000 times, so that it was found that the wear resistance thereof was good. The average crystallite size of the silver-plating film was 109.1 angstroms (10.91 nm).

[Example 4]

[0037] A silver-plated product was produced by the same method as that in Example 3, except that the electroplating (silver-plating) for forming the silver-plating film was carried out at a current density of 7 A/dm^2 for 86 seconds.

[0038] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μ m. The surface analysis of the silver-plating film of this silver-plated product was carried out by the same method as that in Example 2. As a result, the silver-plating film was a film containing 0.3 % by weight of carbon, 0.4 % by weight of sulfur, 0.1 % by weight of nitrogen, 0.3 % by weight of potassium and the balance being silver (Ag purity: 98.9 % by weight) (C/S = 2.2, S/N = 1.3 and C/N = 2.9).

[0039] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 147. It was confirmed that the base material was not exposed after the reciprocating sliding movement was repeated 200 times, so that it was found that the wear resistance thereof was good. The average crystallite size of the silver-plating film was 175.7 angstroms (17.57 nm).

[Comparative Example 1]

[0040] A silver-plated product was produced by the same method as that in Example 1, except that a silver-plating solution of an aqueous solution containing 175 g/L of silver potassium cyanide ($KAg(CN)_2$), 95 g/L of potassium cyanide (KCN) and 70 mg/L of selenium (the aqueous solution containing 94.9 g/L of silver and 38 g/L of free cyanide) was used as the silver-plating solution and that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 18 (±0.5) °C and at a current density of 5 A/dm^2 for 120 seconds.

[0041] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μm. The surface analysis of the silver-plating film of this silver-plated product was carried out by the same method as that in Example 2. As a result, the silver-plating film was a film containing not higher than 0.1 % by weight of carbon and the balance being silver (Ag purity: not less than 99.9 % by weight).

[0042] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 134. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated 80 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 278.0 angstroms (27.80 nm).

[Comparative Example 2]

[0043] A silver-plated product was produced by the same method as that in Example 1, except that a silver-plating solution of an aqueous solution containing 148 g/L of silver potassium cyanide ($KAg(CN)_2$), 140 g/L of potassium cyanide (KCN) and 8 mg/L of selenium (the aqueous solution containing 80.2 g/L of silver and 56 g/L of free cyanide) was used as the silver-plating solution and that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 16 (±0.5) °C and at a current density of 8 A/dm^2 for 75 seconds.

[0044] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μm.

[0045] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 82. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated 50 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 750.0 angstroms (75.00 nm).

[Comparative Example 3]

[0046] A silver-plated product was produced by the same method as that in Example 1, except that a silver-plating solution of an aqueous solution containing 115 g/L of silver potassium cyanide ($KAg(CN)_2$), 60 g/L of potassium cyanide (KCN) and 40 mg/L of selenium (the aqueous solution containing 62.3 g/L of silver and 24 g/L of free cyanide) was used as the silver-plating solution and that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 25 (±0.5) °C and at a current density of 2 A/dm^2 for 300 seconds.

[0047] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μ m.

[0048] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 119. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated 100 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 636.0 angstroms (63.60 nm) .

[Comparative Example 4]

[0049] A silver-plated product was produced by the same method as that in Example 1, except that a silver-plating solution of an aqueous solution containing 40 g/L of silver potassium cyanide ($KAg(CN)_2$), 39 g/L of potassium cyanide (KCN) and 1 g/L of N-allylthiourea (the aqueous solution containing 21.7 g/L of silver and 16 g/L of free cyanide) was used as the silver-plating solution and that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 25 (±0.5) °C and at a current density of 0.7 A/dm^2 for 857 seconds.

[0050] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μ m.

[0051] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 61. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated 30 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 455.6 angstroms (45.56 nm).

[Comparative Example 5]

[0052] A silver-plated product was produced by the same method as that in Example 3, except that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 25 (±0.5) °C and at a current density of 5 A/dm^2 for 120 seconds.

[0053] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μ m. The surface analysis of the silver-plating film of this silver-plated product was carried out by the same method as that in Example 2. As a result, the silver-plating film was a film containing 0.2 % by weight of carbon, 0.3 % by weight of sulfur, 0.1 % by weight of nitrogen, 0.3 % by weight of potassium and the balance being silver (Ag purity: 99.2 % by weight) (C/S = 2.0, S/N = 1.8 and C/N = 3.5).

[0054] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 131. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated not higher than 60 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 257.4 angstroms (25.74 nm).

[Comparative Example 6]

[0055] A silver-plated product was produced by the same method as that in Example 3, except that the electroplating (silver-plating) for forming the silver-plating film was carried out at a liquid temperature of 25 (±0.5) °C and at a current density of 7 A/dm^2 for 86 seconds.

[0056] The thickness of the substantially central portion of the silver-plating film of the silver-plated product thus obtained was measured by the same method as that in Example 1, so that the thickness was 5 μm. The surface analysis of the silver-plating film of this silver-plated product was carried out by the same method as that in Example 2. As a result, the silver-plating film was a film containing 0.1 % by weight of carbon, 0.1 % by weight of sulfur, lower than 0.1 % by weight of nitrogen, 0.1 % by weight of potassium and the balance being silver (Ag purity: not lower than 99.5 % by weight) (C/S = 2.7).

[0057] With respect to the silver-plated product, the measurement of the Vickers hardness HV of the silver-plating film, the evaluation of the wear resistance thereof and the calculation of the crystallite sizes thereof were carried out by the same methods as those in Example 1. As a result, the Vickers hardness HV was 145. It was confirmed that the base material was exposed after the reciprocating sliding movement was repeated not higher than 60 times, so that it was found that the wear resistance thereof was not good. The average crystallite size of the silver-plating film was 269.8 angstroms (26.98 nm).

[0058] The producing conditions and characteristics of the silver-plated products obtained in these examples and comparative examples are shown in Tables 1 through 3.

Table 1

	Silver-Plating Solution						
	$KAg(CN)_2$ (g/L)	KCN (g/L)	MT (g/L)	N-allyl thio urea (g/L)	Se (mg/L)	Ag (g/L)	Free Cyanide (g/L)
Ex. 1	80	39	12.4	-	-	43.4	16
Ex.2	80	39	12.4	-	-	43.4	16
Ex.3	175	95	18.5	-	-	94.9	38
Ex.4	175	95	18.5	-	-	94.9	38
Comp.1	175	95	-	-	70	94.9	38
Comp.2	148	140	-	-	8	80.2	56
Comp.3	115	60	-	-	40	62.3	24
Comp.4	40	39	-	1	-	21.7	16
Comp.5	175	95	18.5	18.5	-	94.9	38
Comp.6	175	95	18.5	-	- -	94.9	38

Table 2

	Silver Plating		
	Liquid Temp. (°C)	Current Density (A/dm^2)	Time (see.)
Ex.1	35	3	200
Ex.2	35	5	120

(continued)

	Silver Plating		
	Liquid Temp. (°C)	Current Density (A/dm^2)	Time (see.)
Ex.3	35	5	120
Ex.4	35	7	86
Comp.1	18	5	120
Comp.2	16	8	75
Comp.3	25	2	300
Comp.4	25	0.7	857
Comp.5	25	5	120
Comp.6	25	7	86

Table 3

	Ag	C	S	N	K	C/S	S/N	G/N
	(% by weight)							
Ex.1	-	-	-	-	-	-	-	-
Ex.2	97.8	0.7	1.1	0.2	0.2	1.7	2.2	3.8
Ex.3	97.7	0.7	0.8	0.3	0.5	2.2	1.3	2.9
Ex.4	98.9	0.3	0.4	0.1	0.3	2.2	1.3	2.9 -
Comp.1	not lower than 99.9	not higher than 0.1	-	-	-	-	-	
Comp.2	-	-	-	-	-	-	-	-
Comp.3	-	- -	-	-	-	-	-	-
Com.4	-	-	-	-	-	-	-	-
Comp.5	99.2	0.2	0.3	0.1	0.3	2.0	1.8	3.5
Comp.6	not lower than 99.5	0.1	0.1	lower than 0.1	0.1	2.7	-	-

Table 4

	Vickers Hardness HV	Number of Durable Times (Number of Times)	Average Crystallite Size (nm)
Ex.1	151	not lower than 1000	6.10
Ex.2	129	not lower than 1000	14.87
Ex.3	129	not lower than 1000	10.91
Ex.4	147	not lower than 200	17.57
Comp.1	134	80	27.80
Comp.2	82	50	75.00
Comp.3	119	100	63.60
Comp.4	61	30	45.66
Comp.5	131	not higher than 60	25.74
Comp.6	145	not higher than 60	26.98

Claims

1. A method for producing a silver-plated product, the method comprising the steps of:

   preparing a silver-plating solution which is an aqueous solution containing silver potassium cyanide, potassium cyanide and a mercaptothiazole; and
   forming a surface layer of silver on a base material by electroplating at a liquid temperature of not lower than 30 °C and at a current density of 1 to 15 A/cm^2 in the silver-plating solution,
   wherein the concentration of the mercaptothiazole in the silver-plating solution is not lower than 5 g/L,

2. A method for producing a silver-plated product as set forth in claim 1, wherein the concentration of the mercaptothiazole in the silver-plating solution is not lower than 10 g/L.

3. A method for producing a silver-plated product as set forth in claim 1 or 2, wherein the concentration of the mercaptothiazole in the silver-plating solution is not higher than 30 g/L.

4. A method for producing a silver-plated product as set forth in any one of claims 1 through 3, wherein the concentration of the mercaptothiazole in the silver-plating solution is not higher than 25 g/L.

5. A method for producing a silver-plated product as set forth in any one of claims 1 through 4, wherein the current density in said electroplating is in the range of from 2 A/cm^2 to 10 A/cm^2.

6. A method for producing a silver-plated product as set forth in any one of claims 1 through 5, wherein the concentration of the silver potassium cyanide in the silver-plating solution is in the range of from 50 g/L to 200 g/L.

7. A method for producing a silver-plated product as set forth in any one of claims 1 through 6, wherein the concentration of the potassium cyanide in the silver-plating solution is in the range of from 20 g/L to 120 g/L.

8. A method for producing a silver-plated product as set forth in any one of claims 1 through 7, wherein the concentration of silver in the silver-plating solution is in the range of from 20 g/L to 120 g/L.

9. A method for producing a silver-plated product as set forth in any one of claims 1 through 8, wherein the concentration of free cyanide in the silver-plating solution is in the range of from 5 g/L to 50 g/L

10. A method for producing a silver-plated product as set forth in any one of claims 1 through 9, wherein said electroplating is carried out at a liquid temperature of not higher than 50 °C,

11. A method for producing a silver-plated product as set forth in any one of claims 1 through 10, wherein said base material is made of copper or a copper alloy.

12. A method for producing a silver-plated product as set forth in any one of claims 1 through 11, wherein an underlying layer of nickel is formed between said base material and said surface layer.

13. A silver-plated product comprising:

    a base material; and
    a surface layer of silver which is formed on the base material, the surface layer having an average crystallite size of not greater than 23 nm and having a Vickers hardness HV of 100 to 160, the surface layer containing not less than 0.3 % by weight of carbon, not less than 0.4 % by weight of sulfur and not less than 0.1 % by weight of nitrogen.

14. A silver-plated product as set forth in claim 13, wherein said surface layer contains 90 to 99 % by weight of silver.

15. A silver-plated product as set forth in claim 13 or 14, wherein said surface layer contains not higher than 2 % by weight of carbon.

16. A silver-plated product as set forth in any one of claims 13 through 15, wherein said surface layer contains not higher than 2 % by weight of sulfur.

17. A silver-plated product as set forth in any one of claims 13 through 16, wherein said base material is made of copper or a copper alloy.

18. A silver-plated product as set forth in any one of claims 13 through 17, wherein an underlying layer of nickel is formed between said base material and said surface layer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/021697

A. CLASSIFICATION OF SUBJECT MATTER

C25D 3/46(2006.01)i; ***C25D 5/12***(2006.01)i; ***C25D 7/00***(2006.01)i; ***H01R 13/03***(2006.01)i
FI: C25D3/46; C25D5/12; C25D7/00 H; H01R13/03 D

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C25D3/00-7/12; H01R13/03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	JP 6916971 B1 (DOWA METALTECH CO., LTD.) 11 August 2021 (2021-08-11) 1-18	1-18
A	WO 2004/048646 A1 (SHINKO ELECTRIC INDUSTRIES CO., LTD.) 10 June 2004 (2004-06-10)	1-18
A	JP 57-43995 A (SUMITOMO DENKI KOGYO KK) 12 March 1982 (1982-03-12)	1-18
A	JP 55-34699 A (LEARONAL, INC.) 11 March 1980 (1980-03-11)	1-18
A	JP 2013-216975 A (ROHM & HAAS ELECTRONIC MATERIALS LLC) 24 October 2013 (2013-10-24)	1-18
A	WO 2016/121312 A1 (DOWA METALTECH CO., LTD.) 04 August 2016 (2016-08-04)	1-18
P, A	WO 2021/171818 A1 (DOWA METALTECH CO., LTD.) 02 September 2021 (2021-09-02)	1-18

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

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Date of the actual completion of the international search **29 July 2022**	Date of mailing of the international search report **09 August 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/021697

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP 6916971 B1	11 August 2021	(Family: none)	
WO 2004/048646 A1	10 June 2004	US 2006/0060474 A1 KR 10-2005-0084783 A CN 1692182 A TW 200427876 A	
JP 57-43995 A	12 March 1982	(Family: none)	
JP 55-34699 A	11 March 1980	US 4247372 A US 4399006 A EP 8919 A1	
JP 2013-216975 A	24 October 2013	US 2013/0256145 A1 DE 102013005499 A1 KR 10-2013-0111454 A CN 103361683 A SG 193763 A TW 201400646 A	
WO 2016/121312 A1	04 August 2016	JP 2020-12202 A US 2017/0370015 A1 US 2020/0048785 A1 EP 3252188 A1 CN 107208297 A CN 109881222 A	
WO 2021/171818 A1	02 September 2021	JP 2021-134425 A	

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 2009079250 A **[0007]**