PLATING SOLUTION, CONDUCTIVE MATERIAL, AND SURFACE TREATMENT METHOD OF CONDUCTIVE MATERIAL

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ABSTRACT
A plating solution including a copper salt, an organic phosphonic acid compound, and at least one compound or ions selected from an amine, α-amino acid, ammonium ions, carboxylic acid ions, carboxylic acid ions, dicarboxylic acid ions, sulfuric acid ions, and thiosulfuric acid ions and a method of treating the surface of a conductive material using this plating solution.
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BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a plating solution, a method of treating the surface of a conductive material using this plating solution, and a conductive material treated on its surface by this surface treatment method.

[0003] 2. Description of the Related Art

[0004] Permanent magnets, which is one type of conductive material, are being widely used for motors and actuators of various types of equipment. As such permanent magnets, Sm—Co-based rare earth permanent magnets obtained by powder metallurgy are being mass produced due to their relatively high performance. However, such Sm—Co-based rare earth permanent magnets have the problem of using as materials the expensive Sm and Co, so end up becoming high in cost.

[0005] Among the rare earth, the smaller atomic weight rare earth elements such as cerium (Ce), praseodymium (Pr), and neodymium (Nd) are present more abundantly than samarium (Sm) and are relatively low in price. Further, iron (Fe) is also inexpensive.

[0006] Therefore, in recent years, relatively inexpensive materials have been used to develop and commercialize Nd—Fe—B-based rare earth permanent magnets having magnetic performances equal to or better than Sm—Co-based rare earth permanent magnets.

[0007] However, such permanent magnets include as main ingredients easily oxidizable rare earth elements and iron, so have relatively low corrosion resistances, are degraded in performance, and have problems in production variance. For this reason, various methods have been proposed for coating the magnet bodies with copper plating films (for example, Japanese Patent Publication (A) No. 60-54406, Japanese Patent Publication (A) No. 1-286407, and Japanese Patent Publication (A) No. 8-3763).

[0008] For example, Japanese Patent Publication (A) No. 60-54406 discloses to plate the surface of an R—Fe—B-based permanent magnet (where, R is a Y element or a rare earth element) with a oxidation resistant plating film so as to suppress the formation of oxides on the surface. Specifically, a Cu-Ni plating is used. By using a copper cyanide solution as the copper base, a superior oxidation resistant permanent magnet is obtained. However, this publication uses copper cyanide for the plating bath, so has the problems of a weak adhesion between the magnet body and the plating film and a lack of reliability.

[0009] On the other hand, Japanese Patent Publication (A) No. 1-286407 discloses electrolytic plating in a copper pyrophosphate plating bath so as to form a copper plating film on the surface of the R—Fe—B-based permanent magnet. However, this publication uses a copper pyrophosphate plating bath, so has the problem that the R—Fe—B-based permanent magnet with the greater tendency for ionization than copper dissolves by immersion and the R—Fe—B-based permanent magnet ends up being corroded at its surface.

[0010] Further, Japanese Patent Publication (A) No. 8-3763 discloses successively treating the surface of a magnet by electrolysis Cu plating, electrolytic Cu plating, and electrolytic Ni and P alloy plating to form multiple plating films and thereby improve the R—Fe—B-based permanent magnet in corrosion resistance. However, a Nd—Fe—B-based permanent magnet suitably used as a rare earth magnet has the property of hydrogen embrittlement, so ends up breaking due to the hydrogen gas produced by the electrolysis Cu plating and therefore a plating film with good pore sealability cannot be obtained.

[0011] As opposed to this, the assignee previously proposed in Japanese Patent No. 3614754 the method of using as the plating solution for forming the Cu plating film a plating solution containing an aliphatic phosphonic acid. With this method, by using a plating solution containing an aliphatic phosphonic acid, it is possible to improve the formability of the Cu plating film and improve the adhesion, corrosion resistance, and heat resistance.

[0012] However, in this Japanese Patent No. 3614754, there is the problem that in the actual production process, if using the same plating solution for repeated plating, the plating solution ends up deteriorating and the color of the Cu changes from a skin color to a dark brown color. For this reason, with the method disclosed in this publication, for example, it is necessary to replace the plating solution with a new solution (a plating solution not previously used for plating) about once every several dozen batches for plating. This has become a cause of higher cost.

SUMMARY OF THE INVENTION

[0013] An object of the present invention is to provide a plating solution able to form a protective film superior in adhesion, corrosion resistance, and heat resistance on the surface of a magnet or other conductive material and able to stably form a protective film having a high adhesion and a good appearance even with repeated plating, a method of treating the surface of a conductive material using this plating solution, and a conductive material obtained by this method.

[0014] The inventors engaged in intensive studies to achieve the above object and as a result discovered that by adding a predetermined compound or ions to a plating solution including a copper salt and organic phosphonic acid compound, the above object can be achieved and thereby completed the present invention.

[0015] That is, the plating solution according to the present invention includes a copper salt,

[0016] an organic phosphonic acid compound, and

[0017] at least one compound or ions selected from an amine, α-amino acid, ammonium ions, carboxylic acid ions, carboxylic acid ions, dicarboxylic acid ions, sulfuric acid ions, and thiosulfuric acid ions.

[0018] In the plating solution of the present invention, the content of the compound or ions is, converted to the compound or ions, preferably 0.01 to 2 mol/liter. If the content of the compound or ions is too low, the effect of the present invention easily becomes small. On the other hand, if too great, uneven plating tends to easily occur.
The plating solution of the present invention is preferably alkaline, specifically preferably has a pH of 8 to 12 in range.

The plating solution of the present invention preferably further includes at least one type of compound selected from a phosphoric acid compound and a hydroxide.

The method of treating the surface of a conductive material according to the present invention comprises using any of the above plating solutions and an anode containing copper for electrolytic plating to form a protective film comprised of copper on the surface of the conductive material.

The conductive material of the present invention is a conductive material obtained by surface treatment by the above method.

In the present invention, the conductive material is not particularly limited so long as it is a material comprised of a material having conductivity, but preferably is a metal, more preferably a metal magnet, furthermore preferably a rare earth magnet. As the rare earth magnet, for example, an R—Fe—B-based rare earth magnet including R (where R is a Y element or a rare earth element), Fe, and B may be mentioned, in particular an Nd—Fe—B-based rare earth permanent magnet may be preferably mentioned.

The plating solution of the present invention contains a copper salt and an organic phosphoric acid compound, so for example when using the plating solution of the present invention and an anode containing copper to form a protective film comprised of copper on the surface of a conductive material, it is possible to form a protective film superior in adhesion and improve the corrosion resistance and heat resistance of the conductive material.

Further, the plating solution of the present invention contains, in addition to the copper salt and organic phosphoric acid compound, the predetermined compound or ions. For this reason, even if repeatedly plating, it is possible to stably form a protective film having a high adhesion and further a good appearance.

Further, the surface treatment method of the present invention uses the plating solution of the present invention and an anode containing copper. For this reason, the conductive material may be stably formed on its surface with a protective film having a high adhesion and further a good appearance.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Below, embodiments of the present invention will be explained. In the present embodiment, the method of treating the surface of a permanent magnet using the plating solution of the present invention will be explained.

Permanent Magnet

First, the permanent magnet, a type of conductive material, will be explained.

The permanent magnet is not particularly limited, but an R—Fe—B-based rare earth magnet including R (where R is one or more rare earth elements including Y), Fe, and B is preferable. In this R—Fe—B-based rare earth magnet, the contents of R, Fe, and B are preferably 5.5 atomic % ≤ R ≤ 30 atomic %, 42 atomic % ≤ Fe ≤ 90 atomic %, 2 atomic % ≤ B ≤ 28 atomic %.

In particular, when producing a permanent magnet by the sintering method, the following composition is preferable.

As R, one or more of Nd, Pr, Dy, Ho, and Tb or further one or more of La, Sm, Ce, Gd, Er, Eu, Pm, Tm, Yb, Lu, and Y is preferably included.

Note that when using two or more elements as R, as the material, it is preferable to use a Misch metal or other mixture.

R has a content of preferably 5.5 to 30 atomic %.

If R is too low in content, the crystal structure of the magnet becomes a cubic crystal structure of the same structure as α-Fe and a high coercive force (Hc) cannot be obtained, while if too great, a R-rich nonmagnetic phase increases and the residual magnetic flux density (Br) falls.

Fe has a content of preferably 42 to 90 atomic %.

If Fe is too low in content, Br drops, while if too great, the Hc falls.

B has a content of preferably 2 to 28 atomic %.

If B is too low in content, the crystal structure of the magnet becomes rhombohedral structure, so the coercive force (Hc) becomes insufficient, while if too great, the B-rich nonmagnetic phase increases and the residual magnetic flux density (Br) falls.

Note that it is possible to replace part of the Fe with Co to improve the temperature characteristic without impairing the magnetic characteristic. In this case, if the amount of Co substitution exceeds 50 atomic % of the Fe, the magnetic characteristic deteriorates, so the amount of Co substitution is preferably 50 atomic % or less.

Further, in addition to R, Fe, and B, the magnet may contain as unavoidable impurities Ni, Si, Al, Cu, Ca, etc. of 3 atomic % of the total or less.

Further, it is possible to substitute part of B by one or more of C, P, S, and Cu to realize an improvement of productivity and lower cost. In this case, the amount of substitution is preferably 4 atomic % of the total or less. Further, for improvement of the coercive force, improvement of the productivity, and reduction of the cost, one or more of Al, Ti, V, Cr, Mn, Bi, Nb, Ta, Mo, W, Sh, Ge, Sn, Zr, Ni, Si, Hf, etc. may be added. In this case, the amount of addition is preferably made, in total, 10 atomic % or less.

The permanent magnet in the present embodiment has a substantially cubic crystal structure main phase. This main phase has a particle size of preferably 1 to 100 μm or so. Further, usually, it includes a nonmagnetic phase of a volume ratio of 1 to 50%.

The permanent magnet is preferably produced by the following powder metallurgy method.

First, the metals or alloy forming the materials are mixed to give the desired composition. Next, the mixed materials are melted in a vacuum or inert gas atmosphere, then cast to obtain an alloy of the desired composition. The casting method is not particularly limited, but for example, the strip cast method etc. may be mentioned. The "Strip cast
method" is the method of supplying the melted liquid state alloy to a roll and continuously casting it into an alloy sheet. The alloy obtained by the casting does not necessarily have to be a single alloy having the final Composition. For example, it may also be a mixture of several types of alloys different in composition. Further, the alloy is not particularly limited in shape. It does not necessarily have to be a sheet and, for example, may also be an ingot.

Then, the obtained alloy is crushed using a jaw crusher etc. to pieces of alloy of 5 to 100 mm square sizes. The obtained pieces of alloy are made to store hydrogen. Next, the hydrogen-storing pieces of alloy are roughly pulverized to obtain alloy powder. Note that in the rough pulverization, by making the pieces of alloy store hydrogen in advance, it is possible to cause pulverization from the surface in a self-decay like manner. After this, the obtained alloy powder is heat treated to remove the hydrogen.

Next, the dehydogenated alloy powder has added to it a pulverization aid in an amount of 0.03 to 0.4 wt % or so. By adding the pulverization aid, it is possible to reduce the amount of residual carbon after sintering and possible to improve the magnetic characteristics. Note that the pulverization aid is not particularly limited, but for example a fatty acid-based compound may be used.

Next, the pulverization aid-containing alloy powder is finely pulverized using a jet mill etc. The fine pulverization is preferably performed until for example the alloy powder is reduced in particle size to 1 to 10 μm or so, in particular to 3 to 6 μm or so.

Next, the finely pulverized powder is shaped, preferably in a magnetic field, to obtain a shaped product. In this case, a magnetic field strength of 400 to 1600 kA/m or so and a shaping pressure of 50 to 500 MPa or so are preferable.

The obtained shaped product is sintered at 1000 to 1200°C for 0.5 to 5 hours and rapidly cooled. After this, it is heat treated, preferably in an inert gas atmosphere, at 500 to 900°C for 1 to 5 hours (aging treatment). Note that the steps before this heat treatment (aging treatment) are preferably performed in a vacuum or in an Ar gas or other nonoxidizing gas atmosphere to prevent oxidation.

When the thus produced permanent magnet has for example an R comprised of Nd, it is particularly superior in magnetic characteristics, and is known to have a negative heat expansion coefficient in a direction perpendicular to the C-axis. The thus obtained permanent magnet is formed on its surface with a protective film comprised of copper using the following plating solution of the present invention.

Below, the method of forming a protective film on the permanent magnet will be explained.

Formation of Protective Film

In the present embodiment, above the permanent magnet is electroplated on its surface using the plating solution of the present invention so as to form a protective film comprised of copper.

Below, the plating solution of the present invention will be explained.

Plating Solution

The plating solution of the present invention includes a copper salt,

an organic phosphonic acid compound, and

at least one type of compound or ions selected from an amine, α-amino acid, ammonium ions, carboxylic acid ions, dicarboxylic acid ions, sulfuric acid ions, and thiocarboxylic acid ions.

The plating solution of the present invention contains, in addition to the copper salt and organic phosphonic acid compound, the predetermined compound or ions, so when forming a protective film comprised of copper on the surface of the permanent magnet, even with repeated plating, it is possible to stably form a protective film high in adhesion and good in appearance.

Note that the reason for this is not necessarily clear, but is believed to be as follows.

In the past, because organic phosphonic acid forms complex with copper ion strongly, the color of the copper ends up deteriorating. As opposed to this, predetermined compound or ions able to ease that phosphonic acid and copper ion form complex exist, dissociating the copper ion is easy and plating with excellent externals becomes possible.

As the predetermined compound (amine, α-amino acid), for example, ethylamine, diethylamine, alanine, glycine, etc. may be mentioned.

Further, as the compound forming the predetermined ions (ammonium ions, carboxylic acid ions, dicarboxylic acid ions, sulfamic acid ions, and thiocarboxylic acid ions), for example, ammonia, carbonic acid, carboxylic acid, dicarboxylic acid, sulfamic acid, thiosulfamic acid and also their salts may be mentioned. Specifically, sodium carbonate, acetate, copper (II) acetate, formic acid, fumaric acid, maleic acid, sodium sulfate, ammonium chloride, ammonium sulfate, oxalic acid, sodium persulfate, etc. may be mentioned. These may be dissolved in the plating solution to form the predetermined ions. Note that the copper (II) acetate generates copper ions in addition to the predetermined ions (acetate ions) in the plating solution. For this reason, this copper (II) acetate also acts as a copper salt.

The content of the compound or ions in the plating solution is, converted to each compound and ions, preferably 0.01 to 2 mol/liter, more preferably 0.1 to 1 mol/liter. If the content of these compounds or ions is too low, the effect of the present invention ends up becoming small. On the other hand, if too great, uneven plating tends to easily occur. Note that for example even when including as the ions bivalent ions (carboxylic acid ions, dicarboxylic acid ions, sulfamic acid ions, thio-compounds acid ions), the content means not the number of moles considering the number of charges of these ions, but the number of moles of these ions themselves.

The copper salt is not particularly limited so long as it dissolves in the plating solution and generates copper ions when the plating solution is completed. As the compound forming this copper salt, in addition to copper salt itself, an oxide of copper, a hydroxide of copper, etc. may be mentioned. Specifically, copper sulfate, copper phosphate, copper chloride, copper phosphonate, or another copper salt or an oxide of copper or hydroxide of copper etc. may be mentioned. The content of the copper salt in the plating solution is, converted to copper ions, preferably 0.1 to 2.0 mol/liter, more preferably 0.2 to 1.0 mol/liter. If the copper salt is too low in content, the protective film tends to become
difficult to form. On the other hand, it the cop salt is too great in content, the ratio of the copper ions not formed into complexes in the plating solution tends to become higher. Note that the content of the copper salt means the content of the copper salt in the plating solution as a whole. That is, for example, when using the copper (II) acetate as the compound forming the acetic acid ions, not only acetic acid ions, but also copper ions are generated in the plating solution. In this case, the content of the copper salt is the content including the copper (II) acetate.

[0067] The organic phosphonic acid compound is not particularly limited, but for example, DL-1-aminoethyl phosphonic acid, 2-aminoethyl phosphonic acid, aminomethyl phosphonic acid, tert-butyl phosphonic acid, diethyl cyanophosphonate, dimethyl phosphonic acid, diethylene triamine pentamethylene phosphonic acid, hydroxyl amino bis(methylenec)phosphonic acid, hexamethylene diamine tetramethylene phosphonic acid, phenyl phosphonic acid, diethyl cyanomethyl-phosphonate, nitrotris(methylene) triphosphonic acid, diethyl phenyl-phosphonate, diethyl vinyl-phosphonate, tetraethyl ethylene-diphosphonate, ethylenediamine tetramethylene phosphonic acid, dimethyl (2-oxoethyl)-phosphonate, dimethyl (2-oxopropyl)-phosphonate, dimethyl allyl-phosphonate, 1,4-butane diphosphonic acid, dimethyl 2-acetoxyethylphosphonate, diethyl 3,3-dimethyl cyclohex-1-enyl-phosphonate, methylene diphosphonic acid, 1-hydroxyethane-1,1-diphosphonic acid, diethyl 3,3-dimethyl-cyclopent-1-enyl-phosphonate, diethyl 3-methylcyclohex-1-enyl-phosphonate, diethyl 3-methylcyclopent-1-enyl-phosphonate, aminomethyl phosphonic acid, (1-aminopropyl)phosphonic acid, (1-aminobutyl)phosphonic acid, (1-aminopentyl)phosphonic acid, (1-aminoethyl) phosphonic acid, (1-amino-3-methylbutyl)phosphonic acid, (1-amino-2-methylpropyl) phosphonic acid, (1-amino-2,2-dimethylpropyl) phosphonic acid, (1-amino-1-methylethyl)phosphonic acid, (1-amino-1-methylpropyl)phosphonic acid, (1-amino-1-methylbutyl)phosphonic acid, (1-amino-1,2-dimethylpropyl) phosphonic acid, (1-amino-1,3-dimethylbutyl)phosphonic acid, (1-amino-1-phenylmethyl)phosphonate, (1-amino-1-cyclopentyl)phosphonic acid, (1-amino-1-cyclohexyl)phosphonic acid, 3-aminopropyl phosphonic acid, diethyl (2-oxo-4-phenylbutyl)-phosphonate, diethyl 3,3-dithioxypropylphosphonate, etc. may be mentioned.

[0068] The content of the organic phosphonic acid compound in the plating solution is preferably 0.1 to 1.0 mol/liter, more preferably 0.3 to 0.6 mol/liter. If the organic phosphonic acid compound is too low in content, the protective film which is formed tends to deteriorate in adhesion. On the other hand, if too great, the plating solution ends up becoming expensive and the production cost ends up increasing as a general trend.

[0069] The plating solution of the present invention may contain, in addition to the above, a phosphoric acid compound or hydroxide.

[0070] The phosphoric acid compound is not particularly limited, but for example potassium pyrophosphate, sodium phosphate, calcium phosphate, etc. may be mentioned.

[0071] The hydroxide is not particularly limited, but for example potassium hydroxide, sodium hydroxide, calcium hydroxide, etc. may be mentioned.

[0072] The content of the phosphoric acid compound, converted to phosphoric acid ions, is preferably 0.03 to 1.0 mol/liter, more preferably 0.1 to 0.5 mol/liter. Further, the content of the hydroxide is preferably 0.5 to 7.0 mol/liter, more preferably 1.0 to 5.0 mol/liter. Note that the above content of the phosphoric acid compound means the content of the phosphoric acid compound in the plating solution. That is, for example, when using copper phosphate as the cop salt, not only copper ions, but also phosphoric acid ions are generated in the plating solution. In this case, the content of the phosphoric acid compound is the content including the copper phosphate.

[0073] The plating solution of the present invention may further contain a brightening agent in an amount of 0 to 10 ml/liter in range. The brightening agent is not particularly limited, but for example various types of organic compound, etc. may be mentioned.

[0074] The plating solution of the present invention is preferably alkaline, specifically has a pH of 8 to 12 in range, more preferably 9.5 to 10.5 in range. By adjusting the plating solution in pH to this range, it is possible to improve the stability of the permanent magnet in the plating solution.

[0075] Electrolytic Plating

[0076] Next, the above plating solution of the present invention and an anode containing copper are used to form a protective film on the surface of the permanent magnet by the barrel plating method or rack plating method etc.

[0077] The anode containing copper is not particularly limited. A copper anode usually used in electrolytic plating may be used. Due to the ease of dissolution of the copper ions, oxygen-free copper, electrolytic copper, phosphorus copper, etc. are preferable.

[0078] Further, as specific plating conditions, the temperature of the plating bath is preferably made 55 to 65°C and the current density at the time of plating is preferably made 0 to 5 A/dm². Further, the thickness of the protective film formed by this copper plating is preferably 1 to 50 μm, more preferably 5 to 20 μm.

[0079] The protective film formed using the plating solution of the present invention is resistant to substitution reactions with the magnetic material at the time of plating and good in adhesion.

[0080] Note that in the present invention, the above-mentioned protective film (hereinafter, in the present embodiment, suitably referred to as the “first protective film”) may if necessary be formed with a second protective film. The second protective film is not particularly limited, but in the present embodiment, it is comprised of an electrolytic nickel plating film or a multilayer film of a copper pyrophosphate plating film and electrolytic nickel plating film.

[0081] When forming an electrolytic nickel plating film, the barrel plating method is preferably used. As the plating bath, the usual wattle bath or nickel sulfamate bath is preferably used. The plating bath has a pH of preferably 3.5 to 6.0, more preferably 4.0 to 5.0, and has a temperature of preferably 40 to 50°C.

[0082] When forming a copper pyrophosphate plating film, the barrel plating method is preferably used. As the
plating bath, the following composition of plating bath is preferably used. This plating bath preferably contains copper pyrophosphate 3 hydrate in an amount of 60 to 110 g/liter, potassium pyrophosphate in 200 to 500 g/liter, ammonia in 1 to 7 g/liter, and a brightening agent in 0 to 5 ml/liter. The plating bath has a pH of preferably 8.0 to 11.0, more preferably 8.5 to 9.5, and has a temperature of preferably 50 to 60°C.

[0083] The second protective film has a thickness or preferably 0.1 to 15 times the thickness of the first protective film.

[0084] The thus surface treated permanent magnet may be suitably used as a part requiring heat resistance and resistance to temperature changes as conditions of use in, for example, automobiles, industrial machinery, etc. or parts requiring heat resistance in the process of production of the parts (for example, resin molding of magnets etc.). Further, this permanent magnet has superior magnetic characteristics even when particularly thin in shape or large in specific area with regard to weight.

[0085] Note that the present invention is not limited to the above embodiment and may be modified in various ways within the scope of the present invention.

[0086] For example, in the above embodiment, as the conductive material of the present invention, a rare earth magnet was illustrated, but the conductive material of the present invention is not limited to a rare earth magnet and may be any conductive material able to be treated on the surface by the plating solution of the present invention.

EXAMPLES

[0087] Below, the present invention will be explained further with reference to detailed examples, but the present invention is not limited to these Examples.

Example 1

[0088] A sintered body having the composition of 14Nd-1Dy-7B-78Fe (numerals indicate atomic ratio) produced by the powder metallurgy method was heat treated in the Ar atmosphere at 600°C for 2 hours, worked to a size of 50x50x5 (mm), and barrel polished to round the edges and obtain a permanent magnet body.

[0089] Next, a sample of this permanent magnet body was washed by an alkaline degreasing solution, then activated at its surface by a 3% nitric acid solution, then washed well by pure water. The sample of this permanent magnet body was then formed on its surface with a protective film by the method explained below.

[0090] First, as the plating bath for forming the protective film, copper sulfate in an amount of 0.2 mol/liter, aminotrimethylene phosphonic acid in 0.6 mol/liter, ammonium sulfate in 0.01 mol/liter, potassium hydroxide in 2 mol/liter, and brightening agents were used to construct a pH 8.0 1-liter plating bath at 60°C.

[0091] Next, this plating bath was used with an electrolyte copper plate as an anode and the above obtained permanent magnet body facing it for plating under a condition of a current density of 1 A/dm² to form a protective film of a thickness of 10 μm. Next, the same plating bath and anode were used under same conditions to plate 100 batches and fabricate 100 samples.

[0092] Among the obtained samples, the first batch sample and 100th batch sample were subjected to a pressure cooker test (P.C.T. test) under conditions of 120°C, 100% RH, 2 atm, and 24 hours to evaluate the corrosion resistance. As a result of the P.C.T. test, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed, i.e., the results were good.

[0093] Further, a first batch sample and 100th batch sample prepared by a method same to the above were used to evaluate the heat resistance. Specifically, first, this first batch sample and 100th batch sample were allowed to stand in a 300°C thermostatic chamber for 1 hour or more for heating, then were allowed to naturally cool to room temperature. Next, such once heated samples and completely unheated samples were magnetized until the saturated state and measured for overall magnetic flux density to investigate the rate of drop in the overall magnetic flux density (the rate in drop of characteristics). The rate in drop of characteristics, in both the first batch sample and 100th batch sample, was 0.01%, i.e., the results were good.

[0094] Further, a first batch sample and 100th batch sample prepared by a method same to the above were used to measure the peeling force to evaluate the protective film adhesion. Specifically, first, each of this first batch sample and 100th batch sample was cut on its surface with two parallel cuts of widths of 10 mm to depths of 30 to 40 μm and lengths of 20 to 30 mm. Further, one ends of these cuts were joined by a cut of a same depth. The peeling force when peeling off only the plating film perpendicular from that part was measured. The peeling force, in both the first batch sample and 100th batch sample, was 50 MPa or more and the adhesion was high, i.e., the results were good.

Example 2

[0095] Except for using a plating bath (pH=9.0) containing copper phosphates in an amount of 0.5 mol/liter, diethylene triamine pentamethylene phosphonic acid in 1.0 mol/liter, sodium carbonate in 0.5 mol/liter, sodium hydroxide in 2 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate of drop of characteristics was 0.01% in each case and, further, the peeling force was 50 MPa or more in each case, i.e., the results were good.

Example 3

[0096] Except for using a plating bath (pH=12) containing copper (II) acetate in an amount of 0.5 mol/liter, diethylene triamine pentamethylene phosphonic acid in 0.1 mol/liter, alanine in 0.5 mol/liter potassium hydroxide in 2 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate of drop of characteristics was 0.01% in each case and, further, the peeling force was 50 MPa or more in each case, i.e., the results were good.
Example 4

[0097] Except for using a plating bath (pH=10) containing copper hydroxide in an amount of 2.0 mol/liter, diethylene triamine pentamethylene phosphonic acid in 1.0 mol/liter, ammonium sulfate in 1.0 mol/liter, potassium hydroxide in 2.0 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate in drop of characteristics was 0.01% in each case and further, the peeling force was 50 MPa or more in each case, i.e., the results were good.

Example 5

[0098] Except for using a plating bath (pH=12) containing copper oxide in an amount of 2.0 mol/liter, diethylene triamine pentamethylene phosphonic acid in 1.0 mol/liter, ammonium sulfate in 2.0 mol/liter, potassium hydroxide in 2.0 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate in drop of characteristics was 0.01% in each case and further, the peeling force was 50 MPa or more in each case, i.e., the results were good.

Example 6

[0099] Except for using a plating bath (pH=8.5) containing copper sulfate in an amount of 1.0 mol/liter, diethylene triamine pentamethylene phosphonic acid in 1.0 mol/liter, potassium phosphate in 1.5 mol/liter, potassium hydroxide in 0.1 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate in drop of characteristics was 0.01% in each case and further, the peeling force was 50 MPa or more in each case, i.e., the results were good.

Example 7

[0100] Except for using a plating bath (pH=9.0) containing copper pyrophosphate in an amount of 0.5 mol/liter, diethylene triamine pentamethylene phosphonic acid in 0.5 mol/liter, sodium thiosulfate in 0.5 mol/liter, fumaric acid in 0.5 mol/liter, potassium hydroxide in 2.0 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance, heat resistance and protective film adhesion. As a result, in both the first batch sample and 100th batch sample, no points of rust or blisters could be observed. Further, the rate in drop of characteristics was 0.01% in each case and further, the peeling force was 50 MPa or more in each case, i.e., the results were good.

Comparative Example 1

[0101] Except for using a copper pyrophosphate plating bath (pH=8.5 plating bath containing copper pyrophosphate 3 hydrate in an amount of 85 g/liter, potassium pyrophosphate in 300 g/liter, ammonia in 3 mol/liter, and brightening agents), the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance. As a result, in both the first batch sample and 100th batch sample, points of rust were observed.

Comparative Example 2

[0102] Except for using a plating bath (pH=7.0) containing copper phosphate in an amount of 0.3 mol/liter, diethylene triamine pentamethylene phosphonic acid in 0.5 mol/liter, potassium hydroxide in 2 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance. As a result, in both the first batch sample, no points of rust or blisters could be observed, but in the 100th batch sample, points of rust were observed.

Comparative Example 3

[0103] Except for using a plating bath (pH=9) containing copper phosphate in an amount of 1.0 mol/liter, diethylene triamine pentamethylene phosphonic acid in 1.0 mol/liter, ammonia in 2.1 mol/liter, potassium hydroxide in 2 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance. As a result, in both the first batch sample and 100th batch sample, points of rust were observed.

Comparative Example 4

[0104] Except for using a plating bath (pH=8) containing copper phosphate in an amount of 2.0 mol/liter, diethylene triamine pentamethylene phosphonate in 1.0 mol/liter, and brightening agents, the same procedure was followed as in Example 1 to plate 100 batches and obtain 100 samples. For each of the obtained samples, the same procedure was followed as in Example 1 to evaluate the corrosion resistance. As a result, in both the first batch sample and 100th batch sample, points of rust were observed.

Evaluation

[0105] From the results of Examples 1 to 7, by using the plating solution of the present invention for plating, it could be confirmed that even with repeated plating, deterioration of the plating solution can be effectively prevented and a protective film with a high adhesion could be stably formed.

[0106] On the other hand, when using a copper pyrophosphate plating bath (comparative Example 1), the first batch and 100th batch sales were each inferior in corrosion resistance.

[0107] Further, when using a plating bath not containing the predetermined compound or ions (Comparative Examples 2 and 4), with repeated plating, the corrosion resistance became inferior.
Further, when the predetermined compound or ions were too great (Comparative Example 3), uneven plating ended up occurring. The first batch and 100th batch samples were each inferior in corrosion resistance.

1. A plating solution including:
   a copper salt,
   an organic phosphonic acid compound, and
   at least one compound or ions selected from an amine, 
   α-amino acid, ammonium ions, carbonic acid ions, 
   carboxylic acid ions, dicarboxylic acid ions, sulfuric 
   acid ions, and thiosulfuric acid ions.
2. The plating solution as set forth in claim 1, wherein the content of said compound or ions is, converted to said compound or ions, 0.01 to 2 mol/liter.

3. The plating solution as set forth in claim 1, wherein said plating solution has a pH of 8 to 12 in range.
4. The plating solution as set forth in claim 1, wherein said plating solution further includes at least one type of compound selected from a phosphoric acid compound and hydroxide.
5. A method of treating the surface of a conductive material comprising using a plating solution as set forth in claim 1 and an anode containing copper for electrolytic plating to form a protective film comprised of copper on the surface of the conductive material.
6. The method of treating the surface of a conductive material as set forth in claim 5 wherein said conductive material is a rare earth magnet.

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