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(54) **ELECTROPLATING SOLUTION COMPOSITION FOR ORGANIC POLYMER-ZINC ALLOY
COMPOSITE PLATING AND PLATED METAL MATERIAL USING SUCH COMPOSITION**

(57) An object of the invention is to provide an electroplating solution composition capable of obtaining a plated film excellent in adhesiveness to a coated film and excellent in corrosion resistance without surface treatment. The present invention relates to an organic polymer composite zinc alloy electroplating solution composition containing: (A) 1 to 600 g/l of Zn ion, (B) 1 to 600

g/l of an iron-group-element ion, and (C) 0.1 to 200 g/l, in terms of W ion, of tungstic acid-based compound, and (D) 0.5 to 500 g/l of water-soluble or water-dispersible organic polymer compound having a number average molecular weight of 1,000 to 1,000,000.

EP 1 719 826 A1

Description

<Technical Field>

[0001] The present invention relates to an organic polymer composite zinc alloy electroplating solution composition for forming an electroplated film having both roles of plating and surface treatment and also to an organic polymer composite zinc alloy electroplated metal material obtainable by electroplating using the composition.

<Background Art>

[0002] As surface treatment of zinc-based plated metal materials for use in automobiles, home electric appliances, building materials, and the like, treatment with a chromate salt and treatment with zinc phosphate are generally conducted but toxicity of chromium has been regarded as a problem. The treatment with a chromium salt has problems that fumes of the chromate salt emit during the treating step, a large cost is required for waste water-treating facility, and chromic acid is eluted out of chemical conversion films. Further, hexavalent chromium compounds are assigned as carcinogenic substances for human by many public institutions including IARC (international Agency for Research on Cancer Review) as a representative and are extremely toxic substances.

[0003] Additionally, in the treatment with zinc phosphate, since rinse treatment with chromic acid is usually conducted after the treatment with zinc phosphate, there arise a problem of chromium treatment and also problems of waste water treatment for a reaction accelerator, metal ions, and the like in a zinc phosphate treating agent and sludge treatment due to elution of metal ions from metals to be treated.

[0004] Furthermore, there is a strong need to reduce a cost for a coating line, so that it is desired to develop a plated film excellent in adhesiveness to a coating film without surface treatment and also excellent in corrosion resistance.

[0005] For these purposes, there have been developed methods of adding a water-soluble organic polymer into a zinc plating bath and co-precipitating the metal and the organic polymer at electroplating a metal material (e.g., see Patent Literatures 1 and 2).

[0006] However, a sufficient corrosion resistance is not obtained by mere addition of a water-soluble organic polymer into a general plating bath and it is difficult to apply the methods to fields wherein a severe corrosion resistance is required, e.g., automobile field.

Patent Literature 1: JP 1-177394 A

Patent Literature 2: JP 7-56080 B

<Disclosure of the Invention>

[0007] An object of the invention is to provide an electroplating solution composition capable of obtaining a plated film excellent in adhesiveness to a coating film without surface treatment and excellent in corrosion resistance.

[0008] As a result of extensive studies for solving the above-described problems, the present inventors have found that corrosion resistance of a plated film is remarkably improved by incorporating an iron-group-element ion and W ion into an organic polymer composite zinc alloy electroplating solution containing Zn ion and a water-soluble and/or water-dispersible organic polymer, and they have accomplished the invention.

[0009] Thus, the invention relates to an organic polymer composite zinc alloy electroplating solution composition containing:

(A) 1 to 600 g/l of Zn ion,

(B) 1 to 600 g/l of an iron-group-element ion,

(C) 0.1 to 200 g/l, in terms of W ion, of tungstic acid-based compound, and

(D) 0.5 to 500 g/l of water-soluble or water-dispersible organic polymer compound having a number average molecular weight of 1,000 to 1,000,000.

[0010] Further, the invention relates to an organic polymer composite zinc alloy electroplated metal material, which is obtainable by electroplating an iron raw material using the above-described organic polymer composite zinc alloy electroplating solution composition.

[0011] Furthermore, the invention relates to a fingerprint-resistant steel plate wherein an organic resin film is directly formed on the organic polymer composite zinc alloy electroplated metal material without surface treatment.

[0012] In addition, the invention relates to a lubricating steel plate wherein an organic resin film having a lubricating function is directly formed on the above-described organic polymer composite zinc alloy electroplated metal material without surface treatment.

<Best Mode for Carrying Out the Invention>

[0013] The organic polymer composite zinc alloy electroplating solution composition (hereinafter referred to as an electroplating solution composition) of the invention contains Zn ion (A), an iron-group-element ion (B), a tungstic acid-based compound (C), and a water-soluble or water-dispersible organic polymer compound (D) as essential components.

"Zn ion (A)"

[0014] The Zn ion as component (A) of the electroplating solution composition of the invention constitutes a main component of the plated layer.

[0015] The Zn ion is added to the plating bath in a form of chloride, sulfate, fluoride, cyanide, oxide, an organic acid salt, a phosphate salt, or elementary metal.

"Iron-group-element ion (B)"

[0016] The iron-group element generally means nickel, cobalt, or iron. The iron-group-element ion as component (B) of the electroplating solution composition of the invention is selected from Ni ion, Co ion, and Fe ion. Of these, Fe ion is preferred in view of corrosion resistance.

[0017] The iron-group-element ion (B) is added to a plating bath in a form of chloride, sulfate, fluoride, cyanide, oxide, an organic acid salt, a phosphate salt, or elementary metal.

"Tungstic acid-based compound (C)"

[0018] The tungstic acid-based compound as component (C) of the electroplating solution composition of the invention can remarkably improve corrosion resistance of the plated layer obtained by combination with an organic polymer compound (D).

[0019] Examples of the tungstic acid-based compound (C) include tungstic acid, tungstate salts, phosphotungstic acid, and phosphotungstate salts. Examples of the salts include ammonium salts, potassium salts, calcium salts, sodium salts, and the like. Particularly, ammonium salts or sodium salts are preferred. Of these, ammonium tungstate, ammonium phosphotungstate, sodium tungstate, and sodium phosphotungstate are preferred in view of corrosion resistance.

"Water-soluble or water-dispersible organic polymer compound (D)"

[0020] The water-soluble or water-dispersible organic polymer compound as component (D) of the electroplating solution composition of the invention is selected from those chemically stable even when it is mixed with the above-described metal ions. By adding the organic polymer compound to the plating solution, adhesiveness between a plated film obtained therefrom and an organic resin film formed on the plated film is remarkably improved and thus a sufficient corrosion resistance can be obtained without chemical conversion treatment of the plated film with a surface treating agent such as zinc phosphate or a chromate.

[0021] As the organic polymer compound (D), those having a water-soluble property or a water-dispersible property (the manner of dispersion may be either suspension or emulsion) can be used. As a method for solubilizing, dispersing, or emulsifying the organic polymer compound in water, a conventionally known method can be used. As the water-soluble or water-dispersible organic polymer compound, preferred are those having at least one hydrophilic group selected from the group consisting of nonionic hydrophilic groups, anionic hydrophilic groups and cationic hydrophilic groups. Specifically, there can be used those containing a functional group independently capable of solubilizing or dispersing it in water (e.g., at least one of a hydroxyl group, a carboxyl group, an amino (imino) group, a sulfonic acid group, a phosphoric acid group, or the like), those neutralized with part or all of those functional groups with an amine compound such as ethanolamine or triethylamine, ammonia water, an alkali metal hydroxide such as lithium hydroxide, sodium hydroxide, or potassium hydroxide in the case of acidic resins such as carboxyl group-containing resins or with a fatty acid such as acetic acid or lactic acid or a mineral acid such as phosphoric acid in the case of basic resins such as amino group-containing resins, and the like.

[0022] Examples of such an organic polymer compound (D) include epoxy resins, phenolic resins, acrylic resins, urethane resins, olefin-carboxylic acid resins, nylon resins, polyvinyl alcohol, resins having a polyoxyalkylene group, polyethylene glycol, polyglycerin, carboxymethyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, and the like.

[0023] As the above-described epoxy resins, use can be preferably made of cationic epoxy resins obtainable by adding an amine to epoxy resins; modified epoxy resins such as acryl-modified ones and urethane-modified ones; and the like. Examples of the cationic epoxy resins include adducts of epoxy compounds with a primary mono- or polyamine, a secondary primary mono- or polyamine, or a primary and secondary mixed polyamine (e.g., see US patent No. 3984299);

adducts of epoxy compounds with a secondary mono- or polyamine having ketiminated primary amino group (e.g., see US Patent No. 4017438); etherified reaction products of epoxy compounds with a hydroxyl compound having a ketiminated primary amino group (e.g., see JP 59-43013 A); and the like.

[0024] As the above-described epoxy compounds, suitable are those having a number average molecular weight of within the range of 400 to 4,000, particularly 800 to 2,000 and an epoxy equivalent of within the range of 190 to 2,000, particularly 400 to 1,000. Such epoxy compounds can be, for example, obtained by reacting polyphenol compounds with epichlorohydrin. Examples of the polyphenol compounds include bis(4-hydroxyphenyl)-2,2-propane, 4,4-dihydroxybenzophenone, bis(4-hydroxyphenyl)-1,1-ethane, bis(4-hydroxyphenyl)-1,1-isobutane, bis(4-hydroxy-tert-butylphenyl)-2,2-propane, bis(2-hydroxynaphthyl)methane, 1,5-dihydroxynaphthalene, bis(2,4-dihydroxyphenyl)methane, tetra(4-hydroxyphenyl)-1,1,2,2-ethane, 4,4-dihydroxydiphenyl sulfone, phenol novolak, cresol novolak, and the like.

[0025] As the phenolic resin, use can be suitably made of a water-solubilized compound from a polymer compound obtained by heating a phenol component and a formaldehyde in the presence of a reaction catalyst to effect addition and condensation. As the above-described phenol component as a starting material, a bifunctional phenol compound, trifunctional phenol compound, or tetrafunctional or polyfunctional phenol compound can be used. Examples thereof include o-cresol, p-cresol, p-tert-butylphenol, p-ethylphenol, 2,3-xyleneol, and 2,5-xyleneol as the bifunctional phenol compounds, phenol, m-cresol, m-ethylphenol, 3,5-xyleneol, and m-methoxyphenol as trifunctional phenol compounds, and bisphenol A, bisphenol F as tetrafunctional phenol compounds. These phenol compounds may be used solely or as a mixture of two or more of them.

[0026] Examples of the above-described acrylic resins include homopolymers or copolymers of monomers each having a hydrophilic group such as a carboxyl group, an amino group, or a hydroxyl group, copolymers of monomers each having a hydrophilic group with the other copolymerizable monomers. They are resins obtainable by emulsion polymerization, suspension polymerization, or solution polymerization and, if necessary, by neutralizing or making it hydrophilic the resulting resins or by modifying the resins.

[0027] Examples of the above-described carboxyl group-containing monomer include acrylic acid, methacrylic acid, maleic acid, maleic anhydride, crotonic acid, itaconic anhydride, and the like.

[0028] Examples of a nitrogen-containing monomer include nitrogen-containing alkyl (meth)acrylates such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, and N-tert-butylaminoethyl (meth)acrylate; polymerizable amides such as acrylamide, methacrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-methylol(meth)acrylamide, N-methoxymethyl(meth)acrylamide, N-butoxymethyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N,N-dimethylaminopropyl(meth)acrylamide, and N,N-dimethylaminoethyl(meth)acrylamide; aromatic nitrogen-containing monomers such as 2-vinylpyridine, 1-vinyl-2-pyrrolidone, and 4-vinylpyridine; allylamine, and the like.

[0029] Examples of the hydroxyl group-containing monomer include monoester compounds of acrylic acid or methacrylic acid with polyhydric alcohols, such as 2-hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, 2,3-dihydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, and poly(ethylene glycol) mono(meth)acrylate; compounds obtained by ring-opening polymerization of ϵ -caprolactone to the above-described monoester compounds of acrylic acid or methacrylic acid with polyhydric alcohols; and the like.

[0030] Examples of the other monomers include alkyl (meth)acrylates having 1 to 24 carbon atoms, such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, n-octyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, octadecyl (meth)acrylate, and isostearyl (meth)acrylate; styrene, vinyl acetate, and the like. These compounds may be used solely or as a mixture of two or more of them. In the invention, "(meth)acrylate" means acrylate or methacrylate.

[0031] As the above-described urethane resins, use can be suitably made of those obtained by chain-extension of polyurethanes each composed of a polyol such as a polyester polyol or a polyether polyol and a diisocyanate in the presence of a chain-extending agent which is a low-molecular-weight compound having two or more active hydrogens, such as a diol or a diamine and by dispersing or dissolving the products stably in water, and known ones can be widely used (e.g., see JP 42-24192 A, JP 42-24194 A, JP 42-5118 B, JP 49-986 B, JP 49-33104 B, JP 50-15027 B, and JP 53-29175 B). As methods for dispersing or dissolving the polyurethane resins stably in water, the following methods can be utilized, for example.

(1) A method of imparting hydrophilicity by introducing an ionic group such as a hydroxyl group, an amino group, or a carboxyl group into the side chain or the terminal of a polyurethane polymer and dispersing or dissolving it in water by self-emulsification.

(2) A method of blocking a reaction-completed polyurethane polymer or a terminal isocyanate group with a blocking agent such as an oxime, an alcohol, a phenol, a mercaptan, an amine, or sodium bisulfite and dispersing the blocked polyurethane polymer in water by force using an emulsifier and a mechanical shear force. Further, a method of mixing a urethane polymer having a terminal isocyanate group with water/an emulsifier/a chain-extending agent and achieving simultaneous dispersion and increase of the molecular weight using a mechanical shear force.

(3) A method of dispersing or dissolving a polyurethane as a water-soluble polyurethane using a water-soluble polyol such as polyethylene glycol as a polyol of a main material for the polyurethane.

[0032] With regard to the above-described polyurethane resin, the abovementioned method of dispersion or dissolution is not limited to a single method and a mixture obtained by each method can be also employed.

[0033] Examples of the diisocyanate usable for synthesis of the above-described polyurethane resins include aromatic, alicyclic and aliphatic diisocyanates, and specifically include hexamethylene diisocyanate, tetramethylene diisocyanate, 3,3'-dimethoxy-4,4'-biphenylene diisocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 1,3-(diisocyanatomethyl)cyclohexanone, 1,4-(diisocyanatomethyl)cyclohexanone, 4,4'-diisocyanatocyclohexanone, 4,4'-methylenebis(cyclohexyl isocyanate), isophorone diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, p-phenylene diisocyanate, diphenylmethane diisocyanate, m-phenylene diisocyanate, 2,4-naphthalene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, and the like. Of these, particularly preferred are 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate.

[0034] Examples of commercial products of the above-described polyurethane resins include HYDRAN HW-330, HW-340, HW-350 (all manufactured by Dainippon Ink And Chemicals, Inc.), SUPERFLEX 100, 150, F-3438D (all manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.), and the like.

[0035] The above-described polyvinyl alcohol resin is preferably polyvinyl alcohol having a saponification degree of 87% or more, particularly so-called completely saponified polyvinyl alcohol having a saponification degree of 98% or more. Further, its number average molecular weight is suitably within the range of 3,000 to 100,000.

[0036] As the above-described resin having a polyoxyalkylene chain, a resin having a polyoxyethylene chain or a polyoxypropylene chain can be suitably used and examples thereof include polyethylene glycol, polypropylene glycol, blocked polyoxyalkylene glycols wherein the polyoxyethylene chain and the polyoxypropylene chain are combined in a block form, and the like.

[0037] As the above-described olefin-carboxylic acid resin, use can be made of at least one water-dispersible or water-soluble resin selected from two kinds, i.e., a copolymer of an olefin such as ethylene or propylene with a polymerizable unsaturated carboxylic acid and a resin obtained by adding a polymerizable unsaturated compound to dispersion of the copolymer to effect emulsion polymerization and further subjecting the product to intraparticle crosslinking.

[0038] The above-described copolymer is a copolymer of an olefin with one or two or more kinds of polymerizable unsaturated carboxylic acids such as (meth)acrylic acid and maleic acid. In the copolymer, it is suitable that the content of the unsaturated carboxylic acid is within the range of 3 to 60% by weight, preferably 5 to 40% by weight and the copolymer can be dispersed in water by neutralizing the acid group in the copolymer with a basic substance.

[0039] The number average molecular weight of the water-soluble or water-dispersible organic polymer compound (D) usable in the invention in terms of polystyrene using a GPC (gel permeation chromatograph) measuring method is within the range of 1,000 to 1,000,000, particularly 2,000 to 500,000 in view of adhesiveness with the organic resin film and storage stability of the plating solution.

[0040] Further, it is preferred to add a complexing agent to the plating solution for the purpose of stabilizing the metal ions in the plating solution. The complexing agent can be selected from the group consisting of oxycarboxylate salts such as citrate salts, tartrate salts, and gluconate salts, aminoalcohols such as monoethanolamine, diethanolamine, and triethanolamine, polyamines such as ethylenediamine (EDA), diethylenetriamine, and triethylenetetramine, amino-carboxylate salts such as ethylenediamine tetraacetate salts and nitroacetate salts, polyhydric alcohols such as sorbit and pentaerythritol, and mixtures thereof.

[0041] In the invention, functions of high corrosion resistance, coating adhesiveness, and the like can be imparted by combining a corrosion-inhibiting pigment and/or ceramic particles capable of being precipitated as discontinuous particles from the electroplating solution.

[0042] As the above-described corrosion-inhibiting pigment, a generally known one can be used and preferred examples thereof include phosphate salts, molybdate salts, metaborate salts, silicate salts, and the like. Further, examples of the ceramic particles include particles of oxides such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , Y_2O_3 , ThO_2 , CeO_2 , and Fe_2O_3 ; carbides such as B_4C , SiC , WC , ZrC , TiC , graphite, and graphite fluoride; nitrides such as BN , Si_3N_4 , and TiN ; borates such as Cr_3B_2 , and ZrB_2 ; silicate salts such as $2\text{MgO}\cdot\text{SiO}_2$, $\text{MgO}\cdot\text{SiO}_2$, and $\text{ZrO}_2\cdot\text{SiO}_2$, and the like. The mixing amount of the corrosion-inhibiting pigment and/or ceramic particles is desirably within the range of 5 to 300 g per liter of the plating bath. Further, the smaller the particle size is, the more excellent dispersion stability is. Therefore, ultrafine particles having a size of 1 μm or less are preferred. Furthermore, it is desirable to control co-precipitated amount in the plating matrix to the range of 1 to 30% by weight, particularly 1 to 10% by weight per total precipitated amount. When the co-precipitated amount is small, an effect of improving corrosion resistance is not exhibited and when it exceeds 30% by weight, plated film becomes brittle and also adhesiveness with the base material decreases, so that the cases are problematic.

[0043] In order to improve corrosion resistance, a corrosion-inhibiting organic compound may be further added to the plating bath. Examples of preferable corrosion-inhibiting organic compound include alkynes, alkynols, amines or salts

thereof, thio compounds, aromatic carboxylic acid compounds or salts thereof, and heterocyclic compounds, and the like.

[0044] Of these, the alkynes mean organic compounds containing a carbon-carbon triple bond and examples thereof include pentyne, hexyne, heptyne, octyne, and the like. The alkynols mean organic compounds having one or more hydroxyl group in the alkynes and examples thereof include propargyl alcohol, 1-hexyn-3-ol, 1-heptyn-3-ol, and the like.

The amines mean organic compounds containing one or more nitrogen atoms in the molecule, which include any of aliphatic or aromatic compounds. Examples of such amines include octylamine, nonylamine, decylamine, laurylamine, tridecylamine, cetylamine, and the like. The thio compounds mean organic compounds containing one or more sulfur atoms in the molecule and examples of such thio compounds include decyl mercaptan, cetyl mercaptan, thiourea, and the like. The heterocyclic compounds mean organic compounds containing atom(s) other than a carbon atom as ring-constituting atoms in a cyclic molecule and examples of such heterocyclic compounds include pyridine, benzothiazole, benzotriazole, quinoline, indole, and the like. Further, examples of the aromatic carboxylic acid compound include benzoic acid, salicylic acid, toluic acid, naphthalenecarboxylic acid, and the like. With regard to the amines or carboxylic acid compounds, it is possible to use a salt thereof, and an equivalent effect can also be obtained thereby. Salts that can be used include, for the case of amines, acid addition salts such as sulfates and hydrochlorides, and for the case of the aromatic carboxylic acid compounds, metal salts such as alkali metal salts and zinc salts, and ammonium salts.

[0045] The amount of the corrosion-inhibiting organic compound to be added to the plating bath is desirably regulated to 0.1 to 10% by weight in the case of the alkynes or alkynols, 3 to 10% by weight in the case of the amines or salts thereof, 0.2 to 5% by weight in the case of the thio compounds, 1 to 10% by weight in the case of the heterocyclic compounds, and 3 to 8% by weight in the case of the aromatic carboxylic acid compounds or salts thereof. Further, it is possible to incorporate, into the plating solution, additive(s) usually used for the purpose of improving burnt deposit at a high current density or throwing power at a low current density. Examples thereof include a reaction product of an amine with an epihalohydrin, polyethylenepolyamine, the other quaternary amine polymer, urea, thiourea, gelatin, polyvinyl alcohol, an aldehyde, and the like.

"Electroplating solution composition"

[0046] The electroplating solution composition of the invention contains Zn ion (A), an iron-group-element ion (B), a tungstic acid-based compound (C), and a water-soluble or water-dispersible organic polymer compound (D) as essential components. Examples of the electroplating bath usable include (1) acidic baths such as a sulfate bath using zinc sulfate, a chloride bath using zinc chloride, and a borofluoride bath using zinc borofluoride, (2) neutral baths wherein zinc chloride is neutralized with ammonia, potassium chloride, or the like, (3) alkaline baths such as a pyrophosphate bath using zinc pyrophosphate, a zincate bath comprising zinc and sodium hydroxide, and the like. With regard to the contents of the components in the electroplating solution composition, suitable is those containing Zn ion (A) of 1 to 600 g/l, preferably 50 to 300 g/l, more preferably 60 to 250 g/l, an iron-group-element ion (B) of 1 to 600 g/l, preferably 50 to 300 g/l, more preferably 60 to 250 g/l, a tungstic acid-based compound (C) of 0.1 to 200 g/l, preferably 5 to 150 g/l, more preferably 10 to 100 g/l in terms of W ion, and a water-soluble or water-dispersible organic polymer compound (D) of 0.5 to 500 g/l, preferably 10 to 300 g/l, more preferably 20 to 200 g/l as solid matter, in view of coated film adhesiveness to a plating and corrosion resistance.

[0047] To the electroplating solution composition of the invention, a complexing agent for stabilizing metal ions, a corrosion-inhibiting pigment and/or ceramic particles capable of being precipitated as discontinuous particles from the electroplating solution for the purpose of further improving corrosion resistance, a corrosion-inhibiting organic compound, and the like can be added. In addition, to the above-described electroplating solution composition, it is possible to use additive(s) usually used for the purpose of improving burnt deposit at a high current density or throwing power at a low current density, such as a pH regulator, a pit inhibitor, a mist suppressant, antifoaming agent, and the like.

[0048] The electroplating solution composition of the invention can form a plated film excellent in coated film adhesiveness, corrosion resistance, and the like through co-precipitation of the organic polymer compound and the metal by electroplating in a similar manner to a conventional method.

[0049] As conditions for electroplating, it is suitable that pH is about 1 to 3 and a bath temperature is about 30 to 80°C in case that the plating bath is a sulfate bath, pH is about 4 to 7 and a bath temperature is about 10 to 50°C in case that the plating bath is a chloride bath, and pH is 12 or higher and a bath temperature is about 10 to 50°C in case that the plating bath is an alkaline bath, and the thickness of the plated film is suitably from about 0.5 to 5 μm in all cases.

"Electroplated metal material"

[0050] The plated metal material of the present invention is obtained by electroplating a metal raw material using the above-described electroplating solution composition. The metal raw material includes materials mainly comprising iron, e.g., materials for automobiles, home electric appliances, and building materials, processed into a shape of a plate, tube, joint, clamp, bolt, nut or the like.

[0051] The electroplating conditions are as described above. Further, the advantages of the invention can be further enhanced by post-treatment with an acidic aqueous solution of a compound containing at least one element selected from the group consisting of cobalt, nickel, titanium, and zirconium after the formation of the electroplated film. As the compound containing at least one element selected from the group consisting of cobalt, nickel, titanium and zirconium, usable examples include oxides, hydroxides, fluorides, complex fluorides, chlorides, nitrates, sulfates, carbonates, etc. of these metals. Specifically, preferred examples thereof include cobalt nitrate, zirconium oxynitrate, titanium hydrofluoride, zirconium hydrofluoride, ammonium titanium hydrofluoride, and ammonium zirconium hydrofluoride.

[0052] The acidic aqueous solutions of the compounds containing these metal elements preferably has a pH falling within the range of from 1 to less than 7, preferably from 3 to 6. The pH can be adjusted by an acid such as hydrochloric acid, nitric acid, sulfuric acid and hydrofluoric acid, or a base such as sodium hydroxide, potassium hydroxide and amines. Further, a complexing agent, silica particles, etc. may be added to the acidic aqueous solution as needed. The amount of the compound containing the metal element to be added is preferably from 0.001 to 5 mol/liter, and particularly preferably about 0.01 to 1 mol/liter.

[0053] The post-treatment with the acidic aqueous solution can be carried out by bringing the electroplated film into contact with the processing solution, for example by immersing the metal material into the processing solution of a bath temperature of 20 to 80°C, preferably 30 to 60°C, for 5 seconds or longer, preferably about 20 to 90 seconds.

[0054] Since the electroplated metal material obtained as above is excellent in coated film adhesiveness, a coating material can be applied directly to the material without particular surface treatment. Further, even when it is combined with a chromium-free environment-responsive surface-treating agent, it exhibits an excellent corrosion resistance.

[0055] The coating material in the case of coating the electroplated metal material of the invention is not particularly limited, any curing mode such as roomtemperature drying, hot curing, or active energy ray-curing can be employed, and any kind of coating materials such as solvent-type coating materials, water-based coating materials, and powdered coating materials may be used. Particularly, in the case that the electroplating solution composition of the invention is applied to automobiles, generally, an electrodeposition paint, an intermediate coat, and a top coat are sequentially applied on the plated film and then baked.

[0056] Since the electroplated metal material of the invention is excellent in corrosion resistance, it is possible that an organic resin film is formed directly on a non-treated tabular electroplated metal material, thereby serving the use as a fingerprint-resistant steel plate. Further, by imparting the lubricating property to the above-described organic resin film, the resulting product can be used as a lubricating steel plate.

[0057] The fingerprint-resistant steel plate is a steel plate having a thin organic resin film formed thereon for preventing generation of rust during the period until the steel plate is used. The organic resin forming the organic resin film is not particularly limited. Examples of suitable resins include polyurethane resins, epoxy resins, acrylic resins, polyester resins, phenolic resins, polyolefin resins, alkyd resins, melamine resins, polybutyral resins, and the like. The organic resin may be a solvent-type resin dissolved in an organic solvent but, if possible, an aqueous resin dissolved or dispersed (suspended or emulsified) in water, particularly an emulsion resin is preferred.

[0058] In the above-described organic film, silica particles may be added in order to improve adhesiveness and corrosion resistance of the film. As the silica particles, water-dispersible colloidal silica is suitable but vapor-phase-process silica and pulverized silica can be also used. There may be mentioned SNOWTEX N, SNOWTEX C, SNOWTEX O (all manufactured by Nissan Chemical Industries, Ltd.), and the like as the water-dispersible colloidal silica and AEROSIL 200V, AEROSIL R-811 (all manufactured by Nippon Aerosil Co., Ltd.), and the like as the other silica particles.

[0059] The lubricating metal material is a steel plate to which a lubricating property is preliminarily imparted, so that processing such as press-molding can be carried out without coating a press oil, for suppressing the use of a solvent unfavorable from the standpoint of global environmental preservation such as chlorofluorocarbon, 1,1,1-trichloroethane used in a press oil-washing step after molding and processing a steel plate. Usually, a lubricating function-imparting agent is incorporated in the organic resin film used for a fingerprint-resistant steel plate or the like, thereby making a lubricating film formed on a steel plate. The lubricating function-imparting agent is preferably an agent which imparts a lubricating (friction coefficient-reducing) function to the film and is not colored by baking. Examples of a preferable lubricating function-imparting agent include polyolefin waxes such as polyethylene and polypropylene; fluorine-based waxes such as tetrafluoroethylene resin (PTFE), chlorotrifluoroethylene resin, vinylidene fluoride resin, vinyl fluoride resin, ethylene/tetrafluoroethylene copolymer resin, and tetrafluoroethylene/hexafluoropropylene copolymer resin, and the like. They may be used solely or as a mixture of two or more of them.

[0060] The thickness of the organic resin film having fingerprint resistance and lubricity is from about 0.5 to 5 μm and may be a colored film containing a dye or pigment. Further, since surface treatment can be omitted, a production process can be remarkably shortened and operating efficiency can be improved by incorporating a coating step for forming the organic resin film into a production line of the electroplated steel plate.

[0061] In the case that the electroplated metal material of the invention is subjected to surface treatment, the treatment can be conducted with a chromate-based surface treating agent or phosphate salt-based surface treating agent. Since the electroplated metal material of the invention is excellent in corrosion resistance, an excellent corrosion resistance

is also exhibited by combination with a chromium-free environment-responsive surface-treating agent such as a zirconium-based surface treating agent or a titanium-based surface-treating agent. In order to reduce an environmental load, preferred is the combination with a chromium-free environment-responsive surface-treating agent.

[0062] The coated metal material can be used in applications where coated metal materials are conventionally used, such as building material, home electric appliances, automobiles, fastening parts, and the like, without particular limitation. The methods for applying the under coat and top coat may be suitably selected according to the application, the shape of an article to be coated, and the like. For example, spraying, dipping, electrodeposition, or the like is suitable in the case of coating of molded articles and roll coating, curtain flow coating, or the like is suitably employed in the case of coating of plate-type articles such as pre-coated metal materials.

<Examples>

[0063] The present invention will be illustrated in greater detail with reference to the following Examples. In this connection, the "part(s)" and "%" used below are all given by weight.

"1. Preparation of plating solution and manufacture of electroplated metal material"

(Examples 1 to 15 and Comparative Examples 1 to 3)

[0064] Each plating solution was obtained according to the blend composition shown in Table 1 below.

[0065] A cold-rolled metal material (SPCC) having a plate thickness of 0.8 mm was subjected to alkaline degreasing and washed with water, and then it was plated under the following conditions using each of the above-described plating solution.

Plating conditions: plating was conducted at a bath temperature of the range of 30 to 60°C using a direct current having a current density of 1 to 30 A/dm². The thickness of a plated film was 3 μm in all cases. The film thickness was measured on a fluorescent X-ray analyzer SEA5200 (manufactured by Seiko Instruments Inc.).

55 50 45 40 35 30 25 20 15 10 5

Table 1

		Metal ion*1 (g/L)					Organic resin*2 (g/l)					Corrosion inhibitor*3 (g/l)			Electro-plated steel plate No.
		Zn	Fe	Co	Ni	W	R1	R2	R3	R4	R5	F1	F2	F3	
Example	1	82	79			10	20								A1
	2	93	60			10		40							A2
	3	78	75			10	20								A2
	4	78	75			20			40						A4
	5	78		75		20				40					A5
	6	78			75	20					120				A6
	7	62	90			20			80						A7
	8	155	150			30		20							A8
	9	232	225			40			40						A9
	10	146	142			60			80						A10
	11	129	125			80	150								A11
	12	112	106			100				200					A12
	13	78	75			10			40			30			A13
	14	78	75			20			40				20		A14
	15	78	75			20			40					1	A15

EP 1 719 826 A1

		Metal ion*1 (g/L)					Organic resin*2 (g/l)					Corrosion inhibitor*3 (g/l)			Electro-plated steel plate No.
		Zn	Fe	Co	Ni	W	R1	R2	R3	R4	R5	F1	F2	F3	
Comparative example	1	90	80			20									B1
	2	170				20		40							B2
	3		170			20			40						B3

*1: Respective metal ions in Table 1 are supplied from the following compounds.
Zn: ZnSO₄·7H₂O
Fe: FeSO₄·7H₂O
Co: CoSO₄·7H₂O
Ni: NiSO₄·7H₂O
W : Na₂WO₄·2H₂O

*2: Respective organic resins in Table 1 are those shown below.
R1: Sodium lignin sulfonate, number average molecular weight of about 10,000.
R2: Na salt of a sulfonated product of a novolak-type phenol resin, number average molecular weight of about 23,000.
R3: Na salt of a sulfonated product of a novolak-type phenol resin, number average molecular weight of about 40,000.
R4: Na salt of a sulfonated product of poly-p-hydroxystyrene, number average molecular weight of about 5,000.
R5: Na salt of a sulfonated product of a bisphenol A-type epoxy resin, number average molecular weight of about 7,000.

*3: Respective corrosion inhibitors in Table 1 are those shown below.
F1: K-WHITE 840E, manufactured by Tayca Corporation, condensed aluminum phosphate.
F2: SNOWTEX-O, manufactured by Nissan Chemical Industries, Ltd., colloidal silica.
F3: 3-Amino-1,2,4-triazole.

"2. Coating system 1"

(Examples 16 to 30 and Comparative Examples 4 to 6)

5 **[0066]** Each surface of the plated metal materials obtained in the above-shown Table 1 was subjected to alkaline degreasing, washed with water, drained, and dried. Thereafter, "MAGICRON 1000 white" (manufactured by Kansai Paint Co., Ltd., an acryl-melamine resin-based coating, white) was applied thereto so that a dry film thickness became 30 μm , and baked at 160°C for 20 minutes to obtain each test coated plate.

10 (Comparative Example 7)

15 **[0067]** To steel plate (SECC material with a plating deposition amount of 20 g/m²: JIS G-3313) having a plate thickness of 0.8 mm and treated with a phosphate salt (trade name: Palbond 3118, manufactured by Nihon Parkerizing Co., Ltd.), "MAGICRON 1000 white" (manufactured by Kansai Paint Co., Ltd., an acryl-melamine resin-based coating, white) was applied thereto so that a dry film thickness became 30 μm , and baked at 160°C for 20 minutes to obtain a test coated plate.

[0068] On respective test coated plates obtained in the above Examples and Comparative Examples, various tests were carried out in accordance with the following test methods. The results are shown in Table 2 below.

20 **[0069]** (Top coat adhesiveness): After each test coated plate was dipped in a boiling water of about 98°C for 2 hours, it was taken out and allowed to stand at room temperature for 2 hours and then the coated surface of the test coated plate was cut by a knife so as to result in each 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 2 mm square were formed. Peeled area of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

- 25 5: No peeling of the coated film is observed.
 4: Peeling of the coated film is observed but peeled area is less than 10%.
 3: Peeled area is from 10% to less than 25%.
 2: Peeled area is from 25% to less than 50%.
 1: Peeled area is 50% or more.

30 **[0070]** (Corrosion resistance after coating): A crosscut reaching the base metal was incised on each test coated plate, which was subjected to salt spray test for 240 hours in accordance with JIS Z-2371. Thereafter, the test coated plate was washed with water and dried. Then, a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

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Table 2

		Electroplated steel plate No.	Test results	
			Top coat adhesiveness	Corrosion resistance after coating (one side, mm)
Example	16	A1	5	3
	17	A2	5	2
	18	A2	5	2
	19	A4	5	2
	20	A5	5	3
	21	A6	5	2
	22	A7	5	4
	23	A8	5	4
	24	A9	5	3
	25	A10	5	2
	26	A11	5	2
	27	A12	5	2
	28	A13	5	2
	29	A14	5	2
	30	A15	5	2
Comparative Example	4	B1	2	5
	5	B2	4	7
	6	B3	5	5
	7		4	7

"3. Coating system 2"

(Examples 31 to 45 and Comparative Examples 8 to 10)

[0071] Each of the plated metal materials obtained in the above-shown Table 1 was subjected to degreasing, washed with water, drained, and dried. Thereafter, a cation-type electrodeposition coating "ELECROTON GT-10" (manufactured by Kansai Paint Co., Ltd., an epoxypolyester resin-based one) was applied by electrodeposition coating and baked at 170°C for 20 minutes to obtain an electrodeposition-coated plate having a dry film thickness of 20 μm. An intermediate coat "AMILAC TP-65 gray" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based one) was applied to the electrodeposition-coated surface using a spray so that a dry film thickness became 30 μm, and baked at 140°C for 20 minutes. Thereafter, a top coat "NEO AMILAC #6000 white" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based one) was applied using a spray so that a dry film thickness became 30 μm, and baked at 140°C for 20 minutes to obtain each test coated plate.

(Comparative Example 11)

[0072] To an alloying hot dip galvanized steel plate (SGCC F06 material: JIS G-3302) having a plate thickness of 0.8 mm and treated with a phosphate salt (trade name: Palbond 3020, manufactured by Nihon Parkerizing Co., Ltd.), a cation-type electrodeposition coating "ELECROTON GT-10" (manufactured by Kansai Paint Co., Ltd., an epoxypolyester resin-based one) was applied by electrodeposition coating and baked at 170°C for 20 minutes to obtain an electrodeposition-coated plate having a dry film thickness of 20 μm. An intermediate coat "AMILAC TP-65 gray" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based one) was applied to the electrodeposition-coated surface using a spray so that a dry film thickness became 30 μm, and baked at 140°C for 20 minutes. Thereafter, a top coat "NEO AMILAC #6000 white" (manufactured by Kansai Paint Co., Ltd., an aminoalkyd resin-based one) was applied using a

EP 1 719 826 A1

spray so that a dry film thickness became 30 μm , and baked at 140°C for 20 minutes to obtain a test coated plate.

[0073] On respective test coated plates obtained in the above Examples and Comparative Examples, various tests were carried out in accordance with the following test methods. The results are shown in Table 3 below.

[0074] (Chipping resistance): A test coated plate was fixed on a test piece holder of a gravel chipping test instrument JA-400 Model (a chipping test apparatus manufactured by Suga Test Instruments Co., Ltd.) at a right angle relative to its gravel spout. Then, the coated surface was blasted with 50 g of crushed granite having a No.7 particle size at -20°C by compressed air of 0.294 MPa (3 kgf/cm²) and generated chips on the coated film were visually observed and evaluated according to the following standards.

AA: The size of chips is considerably small and only the top coat is bruised.

A: The size of chips is small and only the intermediate coat is exposed.

B: The size of chips is small but the metal material of base metal is exposed.

C: The size of chips is considerably large and the metal material of base metal is exposed to a large extent.

[0075] (Water-resistant secondary adhesiveness): After each test coated plate was dipped in warm water of 40°C for 10 days, the coated surface of the test coated plate was cut by a knife so as to result in each 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 2 mm square were formed. Peeled area of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

5: No peeling of the coated film is observed.

4: Peeling of the coated film is observed but peeled area is less than 10%.

3: Peeled area is from 10% to less than 25%.

2: Peeled area is from 25% to less than 50%.

1: Peeled area is 50% or more.

[0076] (Corrosion resistance): A crosscut reaching the base metal was incised on each test coated plate and it was subjected to salt spray test for 960 hours in accordance with JIS Z-2371. Thereafter, the test coated plate was washed with water and air-dried. Then, rust and swelling at a general part were evaluated according to the following standards as well as a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

A: No generation of rust and swelling on the coated surface is observed.

B: Slight generation of rust and swelling on the coated surface is observed.

C: Remarkable generation of rust and swelling on the coated surface is observed.

[0077] (Salt water resistance): A crosscut reaching the base metal was incised on each test coated plate and it was dipped in 5% saline at 50°C for 10 days. Thereafter, the test coated plate was washed with water and air-dried. Then, rust and swelling at a general part were evaluated according to the following standards as well as a cellophane adhesive tape was closely adhered to the crosscut part and a maximum peeled width (one side, mm) from the crosscut part was measured when the tape was peeled off instantaneously.

A: No generation of rust and swelling on the coated surface is observed.

B: Slight generation of rust and swelling on the coated surface is observed.

C: Remarkable generation of rust and swelling on the coated surface is observed.

Table 3

		Electro-plated film No.	Test results					
			Chipping resistance	Water-resistant secondary adhesiveness	Corrosion resistance		Salt water resistance	
					General part	Maximum peeling width (one side, mm)	General part	Maximum peeling width (one side, mm)
Example	31	A1	AA	5	A	6	A	1
	32	A2	AA	5	A	4	A	1
	33	A2	AA	5	A	4	A	1
	34	A4	AA	5	A	4	A	0
	35	A5	AA	5	A	3	A	0
	36	A6	AA	5	A	3	A	0
	37	A7	AA	5	A	5	A	2
	38	A8	AA	5	A	6	A	3
	39	A9	AA	5	A	3	A	0
	40	A10	AA	5	A	3	A	1
	41	A11	AA	5	A	2	A	0
	42	A12	AA	5	A	2	A	1
	43	A13	AA	5	A	2	A	0
	44	A14	AA	5	A	2	A	0
	45	A15	AA	5	A	2	A	0
Comparative Example	8	B1	A	2	A	6	A	2
	9	B2	C	4	A	13	A	4
	10	B3	B	5	A	10	A	3
	11		C	5	A	8	A	2

"4. Coating system 3"

(Examples 46 to 60 and Comparative Examples 12 to 14)

[0078] Each surface of the plated metal materials obtained in the above-shown Table 1 was subjected to alkaline degreasing, washed with water, drained, and dried. Thereafter, a KP color 8000 primer (manufactured by Kansai Paint Co., Ltd., a modified epoxy resin-based coating) was applied thereon by a bar coater so that a dry film thickness became 5 μm , and baked for 20 seconds under conditions so that PMT (maximum reaching temperature of steel plate) became 210°C to form a coated film. Then, a KP color 1580 white (manufactured by Kansai Paint Co., Ltd., a polyester resin-based coating) was applied on the primer film by a bar coater so that a dry film thickness became 15 μm , and baked for 40 seconds under conditions so that PMT became 215°C to manufacture each test coated plate having an upper-layer coated film.

(Comparative Example 15)

[0079] On a hot dip galvanized steel plate (SGCC Z25 material: JIS G-3302) having a plate thickness of 0.8 mm and treated with a chromate (trade name: COSMER 500, manufactured by Kansai Paint Co., Ltd.), a KP color 8000 primer (manufactured by Kansai Paint Co., Ltd., a modified epoxy resin-based coating) was applied by a bar coater so that a dry film thickness became 5 μm , and baked for 20 seconds under conditions so that PMT became 210°C. Then, a KP color 1580 white (manufactured by Kansai Paint Co., Ltd., a polyester resin-based coating) was applied on the primer

film by a bar coater so that a dry film thickness became 15 μm and baked for 40 seconds under conditions so that PMT became 215°C to manufacture each test coated plate having an upper-layer coated film.

[0080] On respective test coated plates obtained in the above Examples and Comparative Examples, tests for coated film adhesiveness, corrosion resistance, and moisture resistance were carried out in accordance with the following test methods. The results are shown in Table 4 below.

[0081] (Coated film adhesiveness): The coated surface of the test coated plate was cut by a knife so as to result in each 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 1 mm square were formed. Peeled degree of the coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

- 5: No peeling of the coated film is observed.
- 4: Peeling of the coated film is observed but peeled area is less than 10%.
- 3: Peeled area is from 10% to less than 25%.
- 2: Peeled area is from 25% to less than 50%.
- 1: Peeled area is 50% or more.

[0082] (Corrosion resistance): After the edge part and rear surface of the test coated plate having an upper-layer coated film, which had been cut into a size of 70 cm x 150 cm, were sealed, there were provided a 4T folded part (a part subjected to a 180° folding, the coated surface being outside and four sheets of a spacer having a thickness of 0.8 mm intervening) at an upper part of the test coated plate and a crosscut part at a lower part of the test coated plate. The coated plate was subjected to salt spray test for 1000 hours in accordance with JIS Z-2371. Then, degree of white rust generation at the 4T folded part, swelling width at the crosscut part, and degree of swelling generation at a general part (a part without processing and cut) were evaluated according to the following standards.

<General part>

[0083]

- AA: No generation of swelling is observed.
- A: Slight generation of swelling is observed.
- B: Considerable generation of swelling is observed.
- C: Generation of swelling is remarkable and part of the coated film is peeled.

<Crosscut part>

[0084]

- AA: One-surface swelling width from crosscut is less than 1 mm.
- A: One-surface swelling width from crosscut is from 1 mm to less than 2 mm.
- B: One-surface swelling width from crosscut is from 2 mm to less than 5 mm.
- C: One-surface swelling width from crosscut is more than 5 mm.

<Folded part>

[0085]

- AA: No generation of white rust is observed.
- A: Slight generation of white rust is observed.
- B: Considerable generation of white rust is observed.
- C: Generation of white rust is remarkable and part of the coated film is peeled.

[0086] (Moisture resistance): After the edge part and rear surface of the test coated plate having an upper-layer coated film, which had been cut into a size of 70 cm x 150 cm, were sealed, a test was carried out in accordance with JIS K-5400 9.2.2. The test time was 1000 hours under conditions of a temperature in a moisture resistance test instrument of 50°C and a relative humidity of 95 to 100%. The degree of swelling generation of the coated film on the test coated plate after the test was evaluated according to the following standards.

- AA: No generation of swelling is observed.

EP 1 719 826 A1

A: Slight generation of swelling is observed.

B: Considerable generation of swelling is observed.

C: Generation of swelling is remarkable and part of the coated film is peeled.

Table 4

		Electro-plated film No.	Test results				
			Coated film adhesiveness	Corrosion resistance			Moisture resistance
				General part	Crosscut part	Folded part	
Example	46	A1	5	AA	A	A	AA
	47	A2	5	AA	A	A	AA
	48	A2	5	AA	A	A	AA
	49	A4	5	AA	AA	A	AA
	50	A5	5	AA	A	A	AA
	51	A6	5	AA	A	A	AA
	52	A7	5	AA	A	A	AA
	53	A8	5	AA	A	A	AA
	54	A9	5	AA	AA	A	AA
	55	A10	5	AA	AA	A	AA
	56	A11	5	AA	A	A	AA
	57	A12	5	AA	A	A	AA
	58	A13	5	AA	A	A	AA
	59	A14	5	AA	A	A	AA
	60	A15	5	AA	A	A	AA
Comparative Example	12	B1	2	AA	B	B	B
	13	B2	4	AA	B	A	A
	14	B3	4	AA	A	B	AA
	15		4	AA	A	B	AA

"5. Coating system 4"

(Examples 61 to 75 and Comparative Examples 16 to 18)

[0087] Each surface of the plated metal materials obtained in the above-shown Table 1 was subjected to degreasing, washed with water, drained, and dried. Thereafter, each of organic resin coating compositions C1 to C5 produced according to the formulations (the formulation ratio is a solid matter ratio) shown in Table 5 below was applied thereon according to the combinations shown in Table 6 so that a dry film weight became 0.8 g/m², and baked for 20 seconds under conditions so that PMT became 120°C to manufacture each test coated plate shown in Table 6.

[0088] The raw materials of respective notes in Table 5 are the following substances, respectively.

* 1) NIKASOL RX-672A: manufactured by Nippon Carbide Industries Co., Inc., an acryl emulsion

* 2) SUPERFLEX 150: manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd., a polyurethane dispersion

* 3) CHEMIPEARL S-650: manufactured by Mitsui Chemicals, Inc., an ethylene ionomer resin

* 4) ADEKA BONTIGHTER HUX232: manufactured by Asahi Denka Co., Ltd., a carboxyl group-containing urethane dispersion

* 5) EPIKOTE 1007: manufactured by Japan Epoxy Resins Co., Ltd., an epoxy resin

EP 1 719 826 A1

- * 6) DURANATE MF-80: manufactured by Asahi Kasei Corporation, a block isocyanate resin
- * 7) SNOWTEX N: manufactured by Nissan Chemical Industries Ltd., colloidal silica
- * 8) AEROSIL R-811: manufactured by Nippon Aerosil Co., Ltd., fine powder silica
- * 9) CHEMIEPEARL W-700: manufactured by Mitsui Chemicals, Inc., a polyethylene dispersion
- * 10) PTFE powder: a polytetrafluoroethylene resin powder having a particle size of 2 to 5 μm

(Comparative Example 19)

[0089] On an electrogalvanized steel plate (SECC material with a plating deposition amount of 20 g/m²: JIS G 3313) having a plate thickness of 0.8 mm and treated with a chromate (trade name: Cosmer 500, manufactured by Kansai Paint Co., Ltd.), an organic resin coating composition C1 shown in Table 5 was applied so that a dry film weight became 0.8 g/m², and baked for 20 seconds under conditions so that PMT became 120°C to manufacture a test coated plate.

Table 5

	Organic resin coating composition No.				
	C1	C2	C3	C4	C5
NIKASOL RX-672A ^{*1)}	75				
SUPERFLEX 150 ^{*2)}		75			
CHEMIEPEARL S-650 ^{*3)}			75		
ADEKA BONTIGHTER HUX232 ^{*4)}				75	
EPIKOTE 1007 ^{*5)}					67.5
DURANATE MF-80 ^{*6)}					7.5
SNOWTEX N ^{*7)}	12.5	12.5	12.5	12.5	
AEROSIL R-811 ^{*8)}					12.5
CHEMIEPEARL W-700 ^{*9)}	12.5	12.5	12.5	12.5	
PTFE powder ^{*10)}					12.5

[0090] On respective test coated plates obtained in the above Examples and Comparative Examples, various tests were carried out in accordance with the following test methods. The results are shown in Table 6 below.

(Test methods)

[0091] (Bare corrosion resistance): After the edge part and rear surface of the test coated plate were sealed, the coated plate was subjected to salt spray test for 360 hours in accordance with JIS Z-2371. Then, the degree of rust on the treated film surface was evaluated according to the following standards.

- A: Degree of white rust generation is less than 5% of the coated film area.
- B: Degree of white rust generation is from 5% to less than 30% of the coated film area.
- C: Degree of white rust generation is 30% or more of the coated film area.

[0092] (Top coat adhesiveness): "MAGICRON #1000 white" (manufactured by Kansai Paint Co., Ltd., an acryl-melamine resin-based coating, white) was applied on the test coated plate so that a dry film thickness became 30 μm , and baked at 150°C for 20 minutes to obtain a top-coat coated plate. After the resulting top-coat coated plate was dipped in a boiling water for 2 hours, it was allowed to stand at room temperature for 2 hours and then the coated surface was cut by a knife so as to result in each 11 cuts reaching the base metal lengthwise and crosswise in a grid pattern, whereby 100 blocks having 1 mm square were formed. The degree of peeling of the top-coat coated film was evaluated according to the following standards at the time when a cellophane adhesive tape was closely adhered to the grid part and the tape was peeled off instantaneously.

- A: No peeling of the upper-layer coated film is observed.
- B: Peeling of the upper-layer coated film is observed in an amount of 1 to 9 blocks.
- C: Peeling of the upper-layer coated film is observed in an amount of 10 or more blocks.

EP 1 719 826 A1

[0093] (Fingerprint resistance): After L value, a value, and b value of the coated film of the test plate were measured using a color-difference meter "SM color computer MODEL SM-5" (manufactured by Suga Test Instruments Co., Ltd.), white vaseline was applied on the coated film. After vaseline was wiped away with a waste cloth, the L value, a value, and b value were again measured. Then, color difference between before and after the vaseline application was calculated and the test plates were evaluated under the following standards.

- A: ΔE is less than 1.0
- B: ΔE is from 1.0 to less than 3.0.
- C: ΔE is 3.0 or more.

[0094] (Lubricity): A plate-like test piece was drawn under a surface pressure of 50 kg/cm² and a drawing rate of 100 m/minute by a tensile testing machine and a coefficient of dynamic friction at that time was determined to evaluate lubricity according to the following standards. In this connection, this test was carried out on the systems wherein C3, C4, and C5, in which a lubricating function-imparting agent was added to each organic resin coating composition, were applied.

- A: Coefficient of dynamic friction is less than 0.15
- B: Coefficient of dynamic friction is from 0.15 to less than 0.30.
- C: Coefficient of dynamic friction is 0.30 or more.

Table 6

		Electro-plated film No.	Organic resincoating composition No.	Test results			
				Bare Corrosion resistance	Top-coat adhesiveness	Finger-print resistance	Lubricity
Example	61	A1	C1	A	A	A	-
	62	A2	C1	A	A	A	-
	63	A2	C2	A	A	A	-
	64	A4	C2	A	A	A	-
	65	A5	C3	A	A	A	A
	66	A6	C3	A	A	A	A
	67	A7	C3	A	A	A	A
	68	A8	C4	A	A	A	A
	69	A9	C4	A	A	A	A
	70	A10	C5	A	A	A	A
	71	A11	C5	A	A	A	A
	72	A12	C5	A	A	A	A
	73	A13	C2	A	A	A	-
	74	A14	C3	A	A	A	A
	75	A15	C5	A	A	A	A
Comparative Example	16	B1	C1	B	C	A	-
	17	B2	C3	B	A	A	A
	18	B3	C5	B	A	A	A
	19		C1	A	B	A	-

"6. Coating system 5"

(Examples 76 to 82)

[0095] A steel bolt was subjected to alkali degreasing and washed with water and then it was dipped in a 1% sulfuric acid solution at room temperature for 30 seconds to effect activation treatment. Thereafter, using a batch-type barrel plating apparatus, plating was conducted in an alkaline plating bath containing predetermined metal ions, a corrosion-inhibiting pigment, a corrosion-inhibiting organic compound, and ceramic particles shown in Table 7. The composition of the film was regulated by changing the concentration ratio of the metal ions in the plating bath, current density, and bath temperature and plated film thickness was controlled by suitably choosing a plating time. Then, post treatment was carried out by dipping it in an acidic aqueous solution comprising 5g/l of HNO_3 and 15 g/l of $(\text{NH}_4)_2\text{ZrF}_6$, whereby a bolt for test was manufactured.

(Comparative Example 20)

[0096] A steel bolt was subjected to alkali degreasing and washed with water and then it was dipped in a 1% sulfuric acid solution at room temperature for 30 seconds to effect activation treatment. Thereafter, electrogalvanizing (5 μm) was conducted using a zincate bath (metal zinc: 10 g/l, sodium hydroxide: 120 g/l). Then, it was dipped in a hexavalent chromium-containing chromate solution manufactured by Yuken Industry Co., Ltd.: METASU CY-6 at 25°C for 10 seconds to effect chromate treatment, whereby a bolt for comparison was manufactured. The attached amount of the chromate film was from 5 to 6 mg/dm^2 .

[0097] Corrosion resistance of the resulting bolt for test was evaluated by the following method. The evaluation results are shown in Table 7.

[0098] (Corrosion resistance): A salt spray test (SST) was carried out in accordance with JIS Z2371 and corrosion resistance was evaluated by the time required for generation of white rust 10% or red rust 5%.

Table 7

		Metal ion* ⁴ (g/L)					Organic resin* ⁵ (g/l)		Corrosion inhibitor* ⁶			Corrosion resistance	
		Zn	Fe	Co	Ni	W	R6	R7	F1	F2	F3	White rust 10%	Red rust 5%
Example	76	78	75			20	20					168	480
	77	93	60			10		20				120	504
	78	93		60		10	20					120	480
	79	93			60	10		20				120	600
	80	78	75			20	20		30			240	720
	81	78	75			20		20		20		240	720
	82	78	75			20	20				1	168	680

(continued)

	Metal ion* ⁴ (g/L)					Organic resin* ⁵ (g/l)		Corrosion inhibitor* ⁶			Corrosion resistance	
	Zn	Fe	Co	Ni	W	R6	R7	F1	F2	F3	White rust 10%	Red rust 5%
Comparative Example 20											72	240
*4: Respective metal ions in Table 7 are supplied from the following compounds. Zn: ZnO Fe: FeSO₄·7H₂O Co: CoSO₄·7H₂O Ni: NiSO₄·7H₂O W : Na₂WO₄·2H₂O *5: Respective organic resins in Table 7 are those shown below. R6: Polyethyleneimine, number average molecular weight of about 3,000. R7: Polyethylene glycol, number average molecular weight of about 10,000. *6: Respective corrosion inhibitors in Table 7 are those shown below. F1: K-WHITE 840E, manufactured by Tayca Corporation, condensed aluminum phosphate. F2: SNOWTEX-O, manufactured by Nissan Chemical Industries, Ltd., colloidal silica. F3: 3-Amino-1,2,4-triazole.												

[0099] While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

[0100] This application is based on Japanese Patent Application Nos. 2003-410843 (filed December 9, 2003) and 2004-149276 (filed May 19, 2004), the contents thereof being herein incorporated by reference.

<Industrial Applicability>

[0101] Since the organic polymer composite zinc alloy electroplated metal material obtainable using the organic polymer composite zinc alloy electroplating solution composition of the invention is excellent in adhesiveness to a coating film to be coated thereon, a sufficient coating adhesiveness and corrosion resistance are obtained without surface treatment such as treatment with a chromate or treatment with a phosphate salt. Thus, not only toxic substances such as a chromium waste solution generated at the surface treatment can be eliminated but also there is a large advantage of cost reduction due to shortening of a coating line.

Claims

1. An organic polymer composite zinc alloy electroplating solution composition containing:

- (A) 1 to 600 g/l of Zn ion,
- (B) 1 to 600 g/l of an iron-group-element ion,
- (C) 0.1 to 200 g/l, in terms of W ion, of tungstic acid-based compound, and
- (D) 0.5 to 500 g/l of water-soluble or water-dispersible organic polymer compound having a number average molecular weight of 1,000 to 1,000,000.

2. The organic polymer composite zinc alloy electroplating solution composition according to claim 1, wherein the iron-group-element ion (B) is Fe ion.

3. The organic polymer composite zinc alloy electroplating solution composition according to claim 1 or 2, wherein the tungstic acid-based compound (C) is at least one compound selected from the group consisting of tungstic acid, tungstate salts, phosphotungstic acid, and phosphotungstate salts.

4. The organic polymer composite zinc alloy electroplating solution composition according to any one of claims 1 to

3, wherein the organic polymer compound (D) has at least one hydrophilic group selected from the group consisting of nonionic hydrophilic groups, anionic hydrophilic groups, and cationic hydrophilic groups.

5. The organic polymer composite zinc alloy electroplating solution composition according to any one of claims 1 to 4, wherein the organic polymer compound (D) has at least one hydrophilic group selected from the group consisting of a hydroxyl group, a sulfonic acid group, a phosphoric acid group, a carboxyl group, an amino group, and an ammonium group.
6. The organic polymer composite zinc alloy electroplating solution composition according to any one of claims 1 to 5, which further contains 5 to 300 g/l of a corrosion-inhibiting pigment and/or ceramic particles.
7. The organic polymer composite zinc alloy electroplating solution composition according to claim 6, wherein the corrosion-inhibiting pigment is at least one selected from the group consisting of phosphate salts, molybdate salts, metaborate salts, and silicate salts.
8. The organic polymer composite zinc alloy electroplating solution composition according to claim 6, wherein the ceramic particles are particles of at least one selected from the group consisting of Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , Y_2O_3 , ThO_2 , CeO_2 , Fe_2O_3 , B_4C , SiC , WC , ZrC , TiC , graphite, graphite fluoride, BN , Si_3N_4 , TiN , Cr_3B_2 , ZrB_2 , $2\text{MgO}\cdot\text{SiO}_2$, $\text{MgO}\cdot\text{SiO}_2$, and $\text{ZrO}_2\cdot\text{SiO}_2$.
9. The organic polymer composite zinc alloy electroplating solution composition according to any one of claims 1 to 8, which further contains 0.01 to 10 g/l of at least one organic compound selected from the group consisting of alkynes, alkynols, amines or salts thereof, thio compounds, aromatic carboxylic acid compounds or salts thereof, and heterocyclic compounds.
10. An organic polymer composite zinc alloy electroplated metal material, which is obtainable by electroplating a metal raw material using the organic polymer composite zinc alloy electroplating solution composition according to any one of claims 1 to 9.
11. The organic polymer composite zinc alloy electroplated metal material according to claim 10, which is obtained by bringing the film formed by the electroplating into contact with an acidic aqueous solution of a compound containing at least one element selected from the group consisting of cobalt, nickel, titanium, and zirconium.
12. A fingerprint-resistant steel plate wherein an organic resin film is directly formed on the organic polymer composite zinc alloy electroplated metal material according to claim 10 or 11 without surface treatment.
13. A lubricating steel plate wherein an organic resin film is directly formed on the organic polymer composite zinc alloy electroplated metal material according to claim 10 or 11 without surface treatment.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/018543

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C25D5/26, C25D3/56, C25D15/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C25D5/26, C25D3/56, C25D15/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2005 Kokai Jitsuyo Shinan Koho 1971-2005 Jitsuyo Shinan Toroku Koho 1996-2005		
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.
X <u>Y</u>	WO 02/052068 A1 (POSCO CO., LTD.), 04 July, 2002 (04.07.02), Full text & KR 002051273 A & JP 2004-518021 A & EP 1346084 A1 & US 2003-64243 A1 & CN 1404536 A	1, 3-5, 10 <u>6-9, 11</u>
X <u>Y</u>	JP 49-11735 A (Toyo Kohan Kabushiki Kaisha), 01 February, 1974 (01.02.74), Full text (Family: none)	1-5, 10, 12, 13 <u>6-9, 11</u>
Y	JP 2001-254195 A (Nippon Steel Corp.), 18 September, 2001 (18.09.01), Claims; Par. Nos. [0018], [0029] to [0041] (Family: none)	6-9
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 07 March, 2005 (07.03.05)		Date of mailing of the international search report 22 March, 2005 (22.03.05)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2004/018543

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	JP 47-16522 B1 (Toyo Kohan Kabushiki Kaisha), 16 May, 1972 (16.05.72), (Family: none)	1-13
A	JP 8-246184 A (ATOTECH USA, INC.), 24 September, 1996 (24.09.96), & EP 727512 A1	1-13
A	JP 2000-309897 A (Sumitomo Metal Industries, Ltd.), 07 November, 2000 (07.11.00), (Family: none)	1-13

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