

SPECIFICATION

AQUEOUS SURFACE-TREATING AGENT FOR METALLIC MATERIAL,
SURFACE-TREATING PROCESS AND SURFACE-TREATED
METALLIC MATERIAL

5

TECHNICAL FIELD

10 This invention relates to an aqueous surface-
treating agent for metallic materials used to form on the
surfaces of sheet coils and moldings made of a metal a
coat having together not only excellent corrosion
resistance and adhesion, but also such heat resistance,
weldability, continuous workability and electric
conductivity as an inorganic coat usually has, and such
fingerprint resistance and paint adhesion as an organic
15 coat usually has; a surface-treating process; and a
surface-treated metallic material. More specifically,
this invention relates to an aqueous surface-treating
agent for metallic materials used to form, on press
working and/or molded products such as car bodies,
20 automotive parts, building materials and parts for
household appliances; cast products; sheet coils; etc.,
made of zinc-containing metal-plated steel sheets, steel
sheets and/or aluminum-containing metallic materials, a
coat having together not only excellent corrosion
25 resistance and adhesion, but also such heat resistance,
weldability, continuous workability and electric
conductivity as an inorganic coat usually has, and such
fingerprint resistance and paint adhesion as an organic
coat usually has; a surface-treating process and a
30 surface-treated metallic material.

BACKGROUND ART

As techniques to form a coat excellent in adhesion
to the surface of metallic materials and giving the

surface corrosion resistance, fingerprint resistance, etc., there have generally been known a process to form a chromate coat using a treating liquid containing chromic acid or dichromic acid or a salt thereof as a main component; a process to form a coat by a phosphate salt treatment; a process to form a coat by treatment only with a silane coupling agent; a process to form a coat of an organic resin; etc., and these processes are put to practical use.

As a technique mainly using an inorganic component, a process is disclosed in JP-A-58-15541 to apply a treating liquid prepared by adding a specific amount of an organic silane coupling agent to a dilute water glass solution or a sodium silicate solution or a mixed solution of them onto a steel and then drying the resulting treating liquid to improve corrosion resistance and paint adhesion.

As a technique mainly using a silane coupling agent, it is taught in US-B-5,292,549 to treat a metallic sheet with an aqueous solution containing an organic functional group-containing silane in a low concentration and a crosslinking agent in order to gain a temporary anticorrosive effect. It is disclosed that the crosslinking agent crosslinks the organic functional group-containing silane to form a dense sioxane coat.

A process is disclosed in JP-A-2001-49453 to form a coat excellent in corrosion resistance and paint adhesion on the surface of a metal using a surface-treating agent containing a compound having two or more alkoxysilane moieties and a compound selected from organic acids, phosphoric acid and complex fluorides.

As a technique using an organic resin coat, a one pack-type aqueous coating agent for steels is disclosed

in JP-A-2001-353750 which contains 5 to 30% by mass of a water-dispersed resin, 0.1 to 20% by mass of silica particles and 0.01 to 20% by mass of an organic titanate compound, respectively as a concentration of solid matter; is excellent in bath stability; is capable of forming a coat excellent in corrosion resistance, solvent resistance, alkali resistance, paint adhesion and coat adhesion; and is suitable for application onto steels such as zinc-containing metal-coated steels and uncoated steels.

There are disclosed in JP-A-2003-105562 a non-chromium-type surface-treated steel sheet excellent in not only corrosion resistance but also fingerprint resistance, blackening resistance and paint adhesion obtained using a surface-treating agent containing a specific resin compound (A), a cationic urethane resin (B) having at least one cationic functional group selected from primary, secondary and tertiary amino groups and quaternary ammonium salt groups, at least one silane coupling agent (C) having a specific reactive functional group and a specific acid compound (E), in which surface-treating agent, the contents of the cationic urethane resin (B) and the silane coupling agent (C) are respectively in the prescribed ranges; and a process for preparation thereof.

DISCLOSURE OF INVENTION

However, techniques disclosed in the above-mentioned JP-A-58-15541, US-B-5,292,549 and JP-A-2001-49453 have problems that performances such as electric conductivity and fingerprint resistance are very poor; it is difficult to further enhance performances such as corrosion resistance and paint adhesion; even if it is possible to form a coat excellent in corrosion resistance and paint

adhesion, there remains a problem in the aspects of environment and safety because of being a solvent-type treating agent; it is difficult to feed the described treating agent stably as an aqueous-type treating agent; etc., and thus have large problems for practical use.

Techniques disclosed in JP-A-2001-353750 and JP-A-2003-105562 have problems that the resulting coated metallic materials are poor in performances such as electric conductivity and spot weldability since corrosion resistance and fingerprint resistance are gained by coating the surface of a metallic material with an organic resin. Further, it is the present state of things that since the main component is an organic polymer and thus thermal decomposition, coloring, viscosity increase, etc. occur in high temperatures, the resulting coated metallic materials cannot be used for heat-resistant uses.

As seen from the above, it is the present state of things that such a surface-treating agent as is usable in place of one giving a chromate coat is not obtained, and development of a surface-treating agent and a surface-treating process capable of generally solving the above problems has strongly been desired.

This invention aims to provide a surface-treating agent for metallic materials which solves the above problems which prior arts have, and is capable of forming a novel coat having together not only excellent corrosion resistance and adhesion, but also such heat resistance, weldability, continuous workability and electric conductivity as an inorganic coat usually has, and such fingerprint resistance and paint adhesion as an organic coat usually has; a surface-treating process using the surface-treating agent; and a metallic material surface-

treated therewith.

The present inventors have intensely studied to solve the above problems, and as a result, they found that a coat having together not only excellent corrosion resistance and adhesion, but also such heat resistance, weldability, continuous workability and electric conductivity as an inorganic coat usually has, and such fingerprint resistance and paint adhesion as an organic coat usually has can be formed by treating a metallic surface with an extremely stable aqueous chemical agent wherein an organic silicon compound having in one molecule a specific functional group (a) and a specific functional group (b) in a specific mutual ratio is compounded; and completed this invention.

Namely, this invention relates to an aqueous metal surface-treating agent wherein an organic silicon compound which has, in one molecule, two or more of functional groups (a) represented by the formula $-\text{SiR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 represent mutually independently alkyl groups, alkoxyl groups or hydroxyl groups, and at least one of them is an alkoxyl group) and at least one hydrophilic functional group (b) selected from hydroxyl groups (which are different from those containable in the functional groups (a)), amino groups, carboxyl groups, phosphoric acid groups, phosphonic acid groups, sulfonic acid groups, polyoxyethylene chains and amido groups, and has a molecular weight, per one functional group (b), of 100 to 10,000, is compounded (Embodiment 1).

The organic silicon compound can generally be formed, for example, by reaction between the following organic compound (A) and the following organic compound (B), but the organic silicon compound and the product by the reaction are not necessarily identical, and can

mutually be different a little, and both can effectively be used in the invention.

Thus, this invention also relates to an aqueous metal surface-treating agent wherein an organic compound
5 (A) having a functional group (I), and an organic compound (B) having a functional group (II) capable of reacting with the functional group (I) and at least one hydrophilic functional group (III) selected from hydroxyl groups (which are different from those containable in the
10 following functional groups (a)), primary, secondary and tertiary amino groups, quaternary ammonium groups, phosphoric acid groups, phosphonic acid groups, sulfonic acid groups, primary amido groups, secondary amido groups and polyoxyethylene chains, all these groups and chains
15 being different from those included in the functional groups (I) and/or the functional groups (II) are compounded, and at least one of the organic compound (A) and the organic compound (B) is an organic silane compound having a functional group (a) represented by the
20 formula $-\text{SiR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 are as defined above) (Embodiment 2).

This invention also relates to a process for surface-treating a metallic material which comprises
25 applying the above surface-treating agent onto the surface of the metallic material, and drying the resulting surface-treating agent to form a coat of 10 to 3,000 mg/m^2 in terms of SiO_2 ; and a metallic material surface-treated by the surface-treating process.

A surface-treated metallic material obtained by
30 applying the surface-treating agent of the invention onto the surface of a metallic material, and drying the resulting surface-treating agent has together not only excellent corrosion resistance and adhesion, but also

such heat resistance, weldability, continuous workability and electric conductivity as an inorganic coat usually has, and such fingerprint resistance and paint adhesion as an organic coat usually has.

5 BEST MODE FOR CARRYING OUT THE INVENTION

 The number of the functional group (a) in the organic silicon compound as an indispensable component of the aqueous metal surface-treating agent (Embodiment 1) of the invention needs to be 2 or more. When the number
10 of the functional group (a) is one, adhesion strength to the surface of a metallic material is lowered. The carbon number of the alkyl group and the alkoxyl group in the definition of R^1 , R^2 and R^3 in the functional group (a) is not particularly limited, but is preferably
15 1 to 6, further preferably 1 to 4 and still further preferably 1 or 2. As the proportion of presence of the functional group (b), the molecular weight of the organic silicon compound per one functional group (b) needs to be 100 to 10,000, and is preferably 200 to 5,000. When the
20 molecular weight per one functional group (b) is less than 100, the water resistance of a coat formed is strikingly lowered. On the other hand, when the molecular weight per one functional group (b) is more than 10,000, the organic silicon compound becomes hard to
25 dissolve or disperse stably.

 The process for preparation of the organic silicon compound in the invention is not particularly limited, and there can, for example, be mentioned (1) a process of obtaining an organic silicon compound by reaction of a
30 compound having two or more active hydrogen-containing functional groups with a chlorosilane, (2) a process of obtaining an organic silicon compound by reaction of a silane coupling agent having a vinyl group with a vinyl

compound copolymerizable with it, (3) a process of obtaining an organic silicon compound by reaction of a silane coupling agent having a specific reactive functional group with a silane coupling agent having at least one reactive functional group capable of reacting with the former reactive functional group, (4) a process of obtaining an organic silicon compound by reaction of a silane coupling agent having a specific reactive functional group with a compound having a functional group reactive with the organic functional group of the silane coupling agent, (5) a process of introducing a hydrophilic group into a multifunctional silane coupling agent, etc.

As to the functional group (b), it is possible to use an organic silicon compound having a functional group (b) in the structure, or it is also possible to react a silane coupling agent having two or more of the functional groups (a) with a compound having a functional group (b) to form an organic silicon compound. As the compound having a functional group (b), there can be mentioned hydroxylamine, polyhydric alcohols, aminethiol, aminesulfonic acid, hydroxyphosphonic acid, amino acids, etc.

The aqueous metal surface-treating agent of the invention (Embodiment 2) is, as mentioned above, an aqueous metal surface-treating agent wherein an organic compound (A) having a functional group (I), and an organic compound (B) having a functional group (II) capable of reacting with the functional group (I) and at least one hydrophilic functional group (III) selected from hydroxyl groups (which are different from those containable in the following functional groups (a)), primary, secondary and tertiary amino groups, quaternary

ammonium groups, phosphoric acid groups, phosphonic acid groups, sulfonic acid groups, primary amido groups, secondary amido groups and polyoxyethylene chains, all these groups and chains being different from those capable of being included in the functional groups (I) and/or the functional groups (II) are compounded, and at least one of the organic compound (A) and the organic compound (B) is an organic silane compound having a functional group (a) represented by the formula $-\text{SiR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 are as defined above).

When the organic compound (B) does not have any hydrophilic functional group (III), or when the aqueous metal surface-treating agent (Embodiment 2) contains only an organic compound (A) having a functional group (I) and a functional group (a) and does not contain the organic compound (B), such organic compound (B) or such organic compound (A) is unstable in an aqueous system or does not dissolve therein, which is an undesirable thing.

When the functional group (I) or functional group (II) is a hydrophilic functional group and a functional group formed after they reacted falls within the definition of the hydrophilic functional group (III), the presence of the hydrophilic functional group (III) is not always necessary. The hydrophilic functional group (III) can be contained from the beginning in the organic compound (B), or can newly be introduced therein.

The organic compound (A) is not particularly limited, and as examples thereof, there can be mentioned epoxy silanes such as 3-glycidyloxypropyltrimethoxysilane, 3-glycidyloxypropylmethyldimethoxysilane and 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane; amino silanes such as N-(2-aminoethyl)-3-aminopropylmethyl-

dimethoxysilane, N-(aminoethyl)-3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane; mercapto silanes such as 3-mercaptopropyl-trimethoxysilane; isocyanato silanes such as 3-isocyanatopropyltrimethoxysilane and 3-isocyanatopropyltriethoxysilane; vinyl group-containing silanes such as vinyltriethoxysilane and p-styryltrimethoxysilane; epoxy compounds such as sorbitol polyglycidyl ethers, polyglycerol polyglycidyl ethers and pentaerythritol polyglycidyl ethers; isocyanate compounds such as tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate and xylylene diisocyanate; methylol group-containing compounds such as melamine and dimethylolpropionic acid; active methylene-containing compounds such as acetoacetoxy acrylate; imido compounds such as N,N'-isopropylcarbodiimide; etc.

The organic compound (B) is not particularly limited, and as examples thereof, there can be mentioned amino silanes such as N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(aminoethyl)-3-aminopropyltrimethoxysilane and 3-aminopropyltriethoxysilane; amine compounds such as isophoronediamine, piperazine, diphenylmethanediamine; polyoxyethylene adducts of epoxy compounds such as neopenytl glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether and hydrogenated bisphenol A diglycidyl ether; hydroxylamines such as ethanolamine and propanolamine; polyhydric alcohols such as glycols; aminethiols such as 2-aminoethanethiol and 2-aminopropanethiol; hydroxycarboxylic acids such as tartaric acid and L-ascorbic acid; aminosulfonic acids such as 2-amino-1-naphthalenesulfonic acid; hydroxyphosphonic acids such as α -glycerophosphonic acid;

diaminoalkylsulfonic acids; amino acids such as glycine, alanine and glutamic acid; etc.

It is preferred that the organic silicon compound or a product formed by the reaction of the organic compound (A) and the organic compound (B) has at least one siloxane bond obtained by condensation of two or more of the functional groups (a). By forming siloxane bond(s) by condensation of two or more of the functional groups (a), the organic silicon compound or the above product comes to have a longer molecular chain and a branch, and, as a result, a coat of network structure becomes easy to form. Further, the reactivity of the silanol is lowered due to steric hindrance, etc., and the stability of the organic silicon compound or the above product in water further increases.

It is preferred to compound a metallic compound (C) containing a bivalent or more metallic ion (when the metallic ion is a Zr ion, a Ti ion, a Hf ion or a Ce ion, the case where the metallic compound (C) is a colloidal dispersoid is excluded) into the aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2), and, thereby, the corrosion resistance of a metallic material treated with the aqueous metal surface-treating agent of the invention increases. It is preferred that the bivalent or more metallic ion is at least one selected from Ti, Zr, Hf, V, Mg, Mn, Zn, W, Mo, Al, Ni, Co and Ca ions. As the compound (C) containing a bivalent or more metallic ion, there can be mentioned salts of such metals with inorganic acids such as fluoro acids, phosphoric acid, nitric acid and sulfuric acid; salts of such metals with organic acids such as formic acid, acetic acid, butyric acid, oxalic acid, succinic acid, lactic acid, L-ascorbic acid, tartaric acid, citric

acid, DL-malic acid, malonic acid, maleic acid and phthalic acid; complex salts of such metals such as alkoxides, alkyl acetonates, alkanediolates, lactates, aminates and stearates thereof. Particularly as V ion-
5 containing compounds, there is no particular limitation, and there can be exemplified vanadium pentoxide V_2O_5 , metavanadic acid HVO_3 , ammonium metavanadate, sodium metavanadate, vanadium oxytrichloride $VOCl_3$, vanadium trioxide V_2O_3 , vanadium dioxide VO_2 , vanadium oxysulfate
10 $VOSO_4$, vanadium oxyacetylacetonate $VO(OC(=CH_2)CH_2COCH_3)_2$, vanadium acetylacetonate $V(OC(=CH_2)CH_2COCH_3)_3$, vanadium trichloride VCl_3 , phosphorusvanadomolybdic acid, etc. When a pentavalent vanadium compound is used, a compound obtained by reducing the valence to tetravalent to
15 bivalent with an organic compound having at least one functional group selected from the group consisting of hydroxyl groups, carbonyl groups, carboxyl groups, primary, secondary or tertiary amino groups, amide groups, phosphoric acid groups and phosphonic acid groups
20 can also be used.

These metallic compounds (C) can be used alone or in a combination of two or more.

These metallic ions are considered to have an effect to increase corrosion resistance by control of the
25 corrosion potential of the metal surface and control of oxidation reduction reaction in a corrosive environment, formation of a very thin coat on the metal surface, increase of the coat density due to crosslinking reaction with functional groups in the coat components, etc.

30 The compounding amount of the metallic compound (C) is preferably such a compounding amount that the mass ratio of the content of the metallic compound (C) to the content of Si derived from the functional group (a) in a

coat obtained from the aqueous metal surface-treating agent, (C)/Si, becomes 0.01 to 10.0, and further preferably such a compounding amount that the mass ratio becomes 0.1 to 5.0. When (C)/Si is less than 0.01, the effect due to the compounding of the metallic compound (C) is not displayed, and thus corrosion resistance is not increased. Whereas, when (C)/Si is more than 10.0, the effect of compounding of the metallic compound (C) is not further increased, and the case is not economical.

It is preferred to compound at least one acid (D) selected from hydrofluoric acid, organic acids and phosphoric acid into the aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2), and, thereby, the corrosion resistance is increased. Hydrofluoric acid increases corrosion resistance by etching effect and further chelating action. Organic acids do not strongly etch metal surfaces because they are acids having a relatively low acidity among acids, but remove uneven very thin oxide coats on the surface and thus increase corrosion resistance. Phosphoric acid forms phosphate conversion coats on metal surfaces although the thickness is very thin, and increases corrosion resistance.

The compounding amount of the acid (D) is preferably such a compounding amount that the mass ratio of the content of the acid (D) to the content of Si derived from the functional group (a) in a coat obtained from the aqueous metal surface-treating agent, (D)/Si, becomes 0.01 to 10.0, and further preferably such a compounding amount that the mass ratio becomes 0.1 to 5.0. When (D)/Si is less than 0.01, the effect due to the compounding of the acid (D) is not displayed, and thus corrosion resistance is not increased. Whereas, when

(D)/Si is more than 10.0, either etching is made excessively and corrosion resistance is lowered, or the effect of compounding of the acid (D) is not further increased and the case is not economical.

5 It is preferred to compound a colloidal dispersion (E) of the simple substance or a compound of at least one element selected from Si, Zr, Ti, Sn, Hf, Ce and Nb into the aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2). These colloidal
10 particles have a concentration gradient in the state of distribution in the coat and are concentrated in the neighborhood of the metal surface to protect the metal surface, and thus, corrosion resistance is heightened. Furthermore, the colloidal particles increase the density
15 of the coat and reduce the coat thickness, and, thus, electric conductivity is heightened, and further, effects of enhancement of the hardness and/or adhesion of the coat, etc. are brought about.

 The compounding amount of the colloidal dispersion
20 (E) is preferably such a compounding amount that the mass ratio of the solid content of the colloidal dispersion (E) to the content of Si derived from the functional group (a) in a coat obtained from the aqueous metal surface-treating agent, (E)/Si, becomes 0.01 to 10.0, and
25 further preferably such a compounding amount that the mass ratio becomes 0.1 to 5.0. When (E)/Si is less than 0.01, the effect due to the compounding of the colloidal dispersion (E) is not displayed. Whereas, when (E)/Si is more than 10.0, the coat is embrittled, and thus,
30 corrosion resistance and adhesion are lowered.

 It is possible to compound a surfactant called a wettability-enhancing agent or a thickener in order to form an even coat on the surface to be coated, an

electric conductivity-enhancing agent, a coloring pigment for enhancement of design properties, an auxiliary agent for enhancement of coating formability, etc. into the aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2). Further, it is also possible to compound, as an agent to give lubricity, an organic lubricant such as polyethylene wax or paraffin wax, a solid lubricant such as graphite, mica or molybdenum disulfide, etc.

It is possible to compound a compound having, in one molecule, at least one functional group selected from the group consisting of at least one unsaturated group selected from the group consisting of C=O groups, C=C groups, C≡C groups, C=N groups, C≡N groups and N=N groups; N-N groups; and S element-containing functional groups, such a compound being called an organic inhibitor, into the aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2), in order to further enhance corrosion resistance. As compounds having such a functional group, there can be mentioned, without limitative intention, C=O group-containing compounds including aldehydes such as formaldehyde and acetaldehyde, ketones such as acetone and methyl ethyl ketone, etc.; C=C group-containing compounds such as benzene and its derivatives, naphthalene and its derivatives, acrylic acid and methacrylic acid and their derivatives, alkyl carboxylic ester and alkylaldehydes; C≡C group-containing compounds such as acetylene alcohol and acetylene derivatives; C=N group-containing compounds such as azines, triazines, osazone dyes, triphenylmethane dyes, chnidin, pyrimidine, pyrazole, imidazole, pyridinium compounds and quinolinium compounds; C≡N group-containing compounds such as ethylene cyanohydrin;

N-N group-containing compounds such as hydrazine compounds and their derivatives; N=N group-containing compounds such as azo dyes; S element-containing compounds such as sulfonic acids, sulfonates, sulfamides, thiourea and cyclic thiourea; etc.

The aqueous metal surface-treating agent of the invention (Embodiment 1 and Embodiment 2) is applied onto the surface of a metallic material and dried with heating to form a coat on the surface of the metallic material. The amount of the coat on the surface of the metallic material is preferably 10 to 3,000 mg/m² in terms of SiO₂.

There is no particular limitation as to metallic materials to which the process of the invention is applied, but zinc-containing metal-plated steel sheets, aluminum sheets and stainless steel sheets are preferred. The surfaces of these metallic materials may previously be subjected to a pretreatment such as phosphate treatment, chromate treatment or the like. There is no particular limitation as to a method to apply the aqueous metal surface-treating agent of the invention onto the surface of a metallic material, and a method such as an immersing method, a spraying method or a roll coating method can be used. There is no particular limitation either as to treatment (coating) temperature and treatment (coating) time, but, generally, treatment (coating) temperature is preferably 10 to 40°C and treatment (coating) time is preferably 0.1 to 10 seconds.

By evaporating the solvent, namely water or the alcohol from the layer of the treating liquid formed on the surface of the metallic material, a coat is formed. For industrially practical formation of a coat, it is preferred to heat drying the layer of the treating liquid. In the occasion, drying temperature is

preferably 30 to 300°C, further preferably 40 to 250°C and still further preferably 60 to 200°C, as a temperature reached by the sheet, and drying time is not particularly limited so long as the above condition of temperature
5 reached by the sheet is met.

When the aqueous metal surface-treating agent of the invention is used, a novel coat having together not only excellent corrosion resistance and adhesion, but also such heat resistance, weldability, continuous workability
10 and electric conductivity as an inorganic coat usually has, and such fingerprint resistance and paint adhesion as an organic coat usually has, can be formed on the surface of a metallic material. The reasons are surmised as follows, but the invention is not limited by such
15 surmise. A coat formed using the aqueous metal surface-treating agent of the invention comprises mainly the organic silicon compound. First, corrosion resistance is surmised to be displayed by remarkable barrier effect brought about by that when part of the organic silicon
20 compound is concentrated by drying, etc., the molecules themselves of organic silicon compound mutually react to form, a continuous coat, and -OR groups formed by hydrolysis of part of the organic silicon compound form Si-O-M bonds (M: metallic element(s) on the surface of
25 the material to be coated) with the metal surface. Furthermore, by that formation of a dense coat becomes possible, it gets possible to make the coat thin and, as a result, electric conductivity becomes good.

Further, it is surmised that a coat formed using the
30 aqueous metal surface-treating agent of the invention has silicon as a base, and as to its structure, the arrangement of silicon-organic chains is regular and the organic chain is relatively short, and thus, silicon-

containing parts and organic parts, namely, inorganic substances and organic substances are arranged regularly and densely in very minute areas in the coat, and, therefore, formation of a novel coat having together such
5 heat resistance, weldability, continuous workability and electric conductivity as an inorganic coat usually has, and such fingerprint resistance and paint adhesion as an organic coat usually has, becomes possible. In this connection, it is ascertained through analysis that, in
10 the silicon-containing parts in the coat, about 80% of the silicon forms sioxane bonds.

Examples

The invention is specifically described below according to examples of the invention and comparative
15 examples, but the invention is not limited thereby. Preparation of test sheets, examples and comparative examples, and processes of application of surface-treating agents for metallic materials are described below.

20 Preparation of test sheets

(1) Materials for tests

The following materials on the market were used.

- Electrogalvanized steel sheet (EG): sheet
25 thickness = 0.8 mm, galvanization amount = 20/20 (g/m²)
- 5% aluminum-containing molten zinc-plated steel sheet (GF): sheet thickness = 0.8 mm, plating amount = 90/90 (g/m²)
- Zinc-nickel alloy-plated steel sheet (Zn/Ni):
30 sheet thickness = 0.8 mm, plating amount = 20/20 (g/m²)
- Hot-dip zinc-plated steel sheet (GI): sheet thickness = 0.8 mm, plating amount = 90/90 (g/m²)
- Hot-dip 55% zinc alloy-plated steel sheet

(GL): sheet thickness = 0.8 mm, plating
amount = 90/90 (g/m²)

· Alloyed (Zn-Fe) Hot-dip zinc-plated steel
sheet (GA): sheet thickness = 0.8 mm, plating
amount = 60/60 (g/m²)

· A-1100 aluminum sheet (AL): sheet
thickness = 0.8 mm

(2) Degreasing treatment

A material was spray treated for 2 minutes
using a silicate alkaline degreasing agent, Fine Cleaner
4336 (registered trade mark: made by Nihon Parkerizing
Co., Ltd.) under the condition of concentration 20 g/L
and temperature 60°C, washed with pure water for
30 seconds and dried, and the resulting material was used
as a test sheet.

Embodiment 1

Preparation of aqueous metal surface-treating
agents, application of the agents onto test sheets and
drying thereof (examples), and preparation of aqueous
metal surface-treating agents for comparison, application
of the agents onto test sheets and drying thereof
(comparative examples)

<Composition A>

Two mols of trimethoxychlorosilane and 1 mol of
trimethylolpropane were reacted in ethanol, the resulting
product solution was mixed with pure water and the
mixture was adjusted so that the solid content became
10%. As to the product, the number of the functional
groups (a) is 2, and the molecular weight per one
functional group (b) is about 530.

<Composition B>

Two mols of vinyltrimethoxysilane and 1 mol of
sulfoethyl acrylate were reacted in ethanol, the

resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 2, and the molecular weight per one functional group (b) is about 320.

<Composition C>

Two mole of 3-glycidoxypropyltrimethoxysilane and 1 mol of 3-aminopropyltriethoxysilane were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 3, and the molecular weight per one functional group (b) is 700.

<Composition D>

Two mole of N-(aminoethyl)-3-aminopropyltrimethoxysilane and 1 mol of 3-isocyanatopropyltrimethoxysilane were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 2, and the molecular weight per one functional group (b) is about 800.

<Composition E>

Four mols of 3-mercaptopropyltrimethoxysilane, 4 mols of 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and 1 mol of dimethylolpropionic acid were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 4, and the molecular weight per one functional group (b) is about 1,900.

<Composition F>

Four mols of 3-glycidoxypropyltrimethoxysilane and

1 mol of ethylenediamine were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 4, and the molecular weight per one functional group (b) is about 500.

<Composition G>

Three mols of 3-aminopropyltriethoxysilane and 1 mol of trimethylolpropane polyglycidyl ether were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 3, and the molecular weight per one functional group (b) is 300.

<Composition H>

Seven mole of 3-mercaptopropyltrimethoxysilane, 1 mol of pentaerythritol polyglycidyl ether and 1 mol of 2-aminopropanethiol were reacted in ethanol, the resulting product solution was mixed with pure water and the mixture was adjusted so that the solid content became 10%. As to the product, the number of the functional groups (a) is 7, and the molecular weight per one functional group (b) is 1,500.

Metallic compound (C)

- C1: Hexafluorotitanic acid
- C2: Titanium alkoxide
- C3: Hexafluorozirconic acid
- C4: Ammonium zirconyl carbonate
- C5: Hexafluorohafnic acid
- C6: Vanadyl acetylacetonate
- C7: magnesium hydrogenphosphate
- C8: Zinc acetylacetonate
- C9: Ammonium metatungstate

C10: Ammonium molybdate
C11: Aluminum hydrogenphosphate
C12: Nickel nitrate
C13: Cobalt nitrate
C14: Cerium nitrate
C15: Calcium hydrogenphosphate

5

10

15

An above compound (C), and an acid (D) and a colloidal dispersion (E) shown in Tables 1 to 3 were appropriately compounded into one of the compositions A to H to prepare an aqueous metal surface-treating agent as an example of Embodiment 1 shown in Tables 1 to 3. The treating agent was adjusted to a solid concentration of 10% with water, bar coater applied onto the surface of a test sheet as shown in Tables 1 to 3 so that the resulting dry coat amount could be 700 mg/m², and dried so that the temperature reached by the sheet could be 80°C to form a coat.

Comparative example 1

20

25

A reactive chromate treatment was made onto a test sheet shown in Tables 4 to 10, and the resulting sheet was immersed in a comparative treating solution obtained by dissolving γ -glycidoxypopyltrimethoxysilane and methanol in deionized water so that the respective concentrations could be 12.0% by mass and 10.0% by mass, and, after draining by a wringer roll, dried so that the temperature reached by the sheet could be 80°C to form a coat.

Comparative example 2

30

A comparative treating solution obtained by dissolving γ -glycidoxypopyltrimethoxysilane and methanol in deionized water so that the respective concentrations could be 5.0% by mass and 10% by mass, was applied onto the surface of a test sheet using a No. 3 bar coater, and

dried so that the temperature reached by the sheet could be 80°C to form a coat.

Comparative example 3

5 A comparative treating solution obtained by dissolving ammonium zirconium carbonate, ammonium phosphate and vanadyl acetylacetonate in water so that the respective concentrations could be 2.0 g/L, 2.0 g/L and 0.5 g/L was applied onto the surface of a test sheet using a No. 3 bar coater, and dried so that the
10 temperature reached by the sheet could be 80°C to form a coat.

Comparative example 4

A comparative treating solution obtained by dispersing an ionomer resin, a water soluble
15 multifunctional epoxy group-containing compound and an ammonium ion-adsorbing silica in water so that the respective concentrations could be 4.0 g/L, 0.5 g/L and 0.5 g/L was applied onto the surface of a test sheet using a No. 3 bar coater, and dried so that the
20 temperature reached by the sheet could be 80°C to form a coat.

Embodiment 2

Preparation of aqueous metal surface-treating agents, application of the agents onto test sheets and drying thereof (examples), and preparation of aqueous metal surface-treating agents for comparison, application of the agents onto test sheets and drying thereof (comparative examples)
25

Organic compound (A)

30 A1: 3-Glycidoxypopyltrimethoxysilane
A2: 3-Aminopropyltrimethoxysilane
A3: 3-Mercaptopropyltrimethoxysilane
A4: 3-Isocyanatopropyltrimethoxysilane

A5: Pentaerythritol polyglycidyl ether

A6: Diphenylmethane diisocyanate

A7: Melamine

A8: Dimethylolpropionic acid

5 A9: N,N-Diisopropylcarbodiimide

Organic compound (B)

B1: N-(aminoethyl)-3-aminopropyltrimethoxysilane

B2: Diphenylmethanediamine

10 B3: Neopentyl glycol polyglycidyl ether
polyoxyethylene adduct

B4: Glycerol

B5: Diaminoalkylsulfonic acid

B6: α -glycerophosphoric acid

Metallic compound (C)

15 The same as mentioned in Embodiment 1

An above organic compound (A), an above organic compound (B), an above metallic compound (C), and an acid (D) and a colloidal dispersion (E) shown in Table 11 were appropriately compounded into water to prepare an aqueous
20 metal surface-treating agent as an example of Embodiment 2 shown in Table 11. The treating agent was adjusted to a solid concentration of 10% with water, bar coater applied onto the surface of a test sheet as shown in Tables 12 to 18 so that the resulting dry coat amount
25 could be 700 mg/m², and dried so that the temperature reached by the sheet could be 80°C to form a coat.

Comparative example 1

A reactive chromate treatment was made onto a test sheet, and the resulting sheet was immersed in a
30 comparative treating solution obtained by dissolving γ -glycidoxypropyltrimethoxysilane and methanol in deionized water so that the respective concentrations could be 12.0% by mass and 10.0% by mass, and, after draining by a

wringer roll dried so that the temperature reached by the sheet could be 80°C to form a coat.

Comparative example 2

5 A comparative treating solution obtained by dissolving γ -glycidoxypropyltrimethoxysilane and methanol in deionized water so that the respective concentrations could be 5.0% by mass and 10% by mass, was applied onto the surface of a test sheet using a No. 3 bar coater, and dried so that the temperature reached by the sheet could
10 be 80°C to form a coat.

Comparative example 3

A comparative treating solution obtained by dissolving ammonium zirconium carbonate, ammonium phosphate and vanadyl acetylacetonate in water so that
15 the respective concentrations could be 2.0 g/L, 2.0 g/L and 0.5 g/L was applied onto the surface of a test sheet using a No. 3 bar coater, and dried so that the temperature reached by the sheet could be 80°C to form a coat.

20 Comparative example 4

A comparative treating solution obtained by dispersing an ionomer resin, a water soluble multifunctional epoxy group-containing compound and an ammonium ion-adsorbing silica in water so that the
25 respective concentrations could be 4.0 g/L, 0.5 g/L and 0.5 g/L was applied onto the surface of a test sheet using a No. 3 bar coater, and dried so that the temperature reached by the sheet could be 80°C to form a coat.

30 Evaluation tests (Common to Embodiment 1 and Embodiment 2)

(1) Corrosion resistance at the plane part

A salt spray test according to JIS-Z-2371 was

made for 120 hours, and thereby, the state of incidence of white rust was observed.

<Evaluation criterion>

5 ◎ = The proportion of incidence of white rust is less than 3% of the whole area

○ = The proportion of incidence of white rust is 3% or more but less than 10% of the whole area

△ = The proportion of incidence of white rust is 10% or more but less than 30% of the whole area

10 × = The proportion of incidence of white rust is 30% or more of the whole area

(2) Corrosion resistance at the wrought part

An Erichsen test (extrusion: 7 mm) was made, and, then, a salt spray test according to JIS-Z-2371 was made for 72 hours, and thereby, the state of incidence of white rust was observed.

<Evaluation criterion>

◎ = The proportion of incidence of white rust is less than 10% of the whole area

20 ○ = The proportion of incidence of white rust is 10% or more but less than 20% of the whole area

△ = The proportion of incidence of white rust is 20% or more but less than 30% of the whole area

25 × = The proportion of incidence of white rust is 30% or more of the whole area

(3) Electric conductivity

The surface insulation resistance of a coating was measured using a device for measuring the surface insulation resistance

30 <Evaluation criterion>

◎ = The electric resistance is less than 1.0Ω

○ = The electric resistance is 1.0Ω or more

but less than 2.0Ω

Δ = The electric resistance is 2.0Ω or more
but less than 3.0Ω

$\times$ = The electric resistance is 3.0Ω or more

5 (4) Heat resistance

A test sheet was heated at 200°C for 2 hours in an oven, and, then, subjected to a salt spray test according to JIS-Z-2371, and thereby, the state of incidence of white rust was observed.

10 <Evaluation criterion>

$\odot$ = The proportion of incidence of white rust is less than 3% of the whole area

$\circ$ = The proportion of incidence of white rust is 3% or more but less than 10% of the whole area

15 Δ = The proportion of incidence of white rust is 10% or more but less than 30% of the whole area

$\times$ = The proportion of incidence of white rust is 30% or more of the whole area

(5) Fingerprint resistance

20 A test sheet was coated with a vaseline, and the gain and loss of the L value (ΔL) between before and after the coating was measured by a color difference meter.

<Evaluation criterion>

25 $\odot$ = ΔL is less than 0.5

$\circ$ = ΔL is 0.5 or more but less than 1.0

Δ = ΔL is 1.0 or more but less than 2.0

$\times$ = ΔL is 2.0 or more

(6) Stability

30 A treating agent was allowed to stand in a constant temperature chamber of 40°C , the stability of the

agent was evaluated by days which elapsed until the agent gels.

<Evaluation criterion>

⊙ = There is no gelation

5 ○ = Gelation days are 90 days or more but less than 120 days

△ = Gelation days are 60 days or more but less than 90 days

× = Gelation days are less than 60 days

10 Results of the evaluation tests

 The results of the tests as to Embodiment 1 are shown in Tables 4 to 10. It is seen that the treating agents of Examples 1 to 56 in Tables 1 to 3 display corrosion resistance equal to that of the chromate,
15 electrical conductivity and heat resistance equal to or more than those of the inorganic system and fingerprint resistance equal to that of the organic systems, and are extremely stable.

 The results of the tests as to Embodiment 2 are
20 shown in Tables 12 to 18. It is seen that the treating agents of Examples 1 to 15 in Table 11 display corrosion resistance equal to that of the chromate, electrical conductivity and heat resistance equal to or more than those of the inorganic system and fingerprint resistance
25 equal to that of the organic systems, and are extremely stable.

Table 1 Examples of Embodiment 1

No.	Test sheet	Composition	Metallic compound (C)		Acid (D)		(D)/Si		Colloidal dispersion (E)	
				(C)/Si				(D)/Si		(E)/Si
No. 1	EG	A	C1	0.01	Hydrofluoric acid		1.0		SiO ₂	5
No. 2		B	C2	2.4	Phosphoric acid		3.5		ZrO ₂	3.5
No. 3		C	C3	0.07	Phosphoric acid		0.3		-	-
No. 4		D	C4	0.03	Phosphoric acid		4.2		TiO ₂	2
No. 5		E	C5	3.1	Ascorbic acid		9.4		Sn	2
No. 6		F	C6	0.1	Hydrofluoric acid		2.4		-	-
No. 7		G	C7	1.2	Hydrofluoric acid		3.2		-	-
No. 8		H	C8	0.3	Citric acid		0.5		Hf	2.5
No. 9	GF	A	C9	0.15	Phosphoric acid		0.0		Ce	2
No. 10		B	C10	2.2	Hydrofluoric acid		3.4		-	-
No. 11		C	C11	3.4	Phosphoric acid		5.4		-	-
No. 12		D	C12	8.4	Hydrofluoric acid		6.1		-	-
No. 13		E	C13	2.6	Tartaric acid		3.8		-	-
No. 14		F	C14	0.1	Phosphoric acid		2.1		-	-
No. 15		G	C15	3.6	Hydrofluoric acid		6.1		Nb	1
No. 16		H	C1	2.8	Malonic acid		1.0		SiO ₂	3.5
No. 17	ZN	A	C2	6.4	Phosphoric acid		4.8		ZrO ₂	5
No. 18		B	C3	6.4	Phosphoric acid		2.4		TiO ₂	5
No. 19		C	C4	3.2	-		-		-	-
No. 20		D	C5	2.7	Hydrofluoric acid		1.1		Sn	2.5
No. 21		E	C6	9.4	Butyric acid		5.9		Hf	3
No. 22		F	C7	2.4	Hydrofluoric acid		3.4		Ce	0.1
No. 23		G	C8	3.1	Hydrofluoric acid		2.2		Nb	0.5
No. 24		H	C9	2.8	Phosphoric acid		8.4		-	-

Table 2 Examples of Embodiment 1

No.	Test sheet	Composition	Metallic compound (C)		Acid (D)		Colloidal dispersion (E)	
				(C)/Si		(D)/Si		(E)/Si
No. 25	GI	A	C10	5.4	Succinic acid	6.1	SiO ₂	2
No. 26		B	C11	2.4	Hydrofluoric acid	3.1	ZrO ₂	2.5
No. 27		C	-	-	-	-	-	-
No. 28		D	C13	0.05	Phosphoric acid	2.1	TiO ₂	3
No. 29		E	C14	0.04	Lactic acid	5.8	Sn	3
No. 30		F	C15	2.4	Hydrofluoric acid	4.8	Hf	3.5
No. 31		G	C1	0.5	Hydrofluoric acid	3.4	Ce	3
No. 32		H	C2	9.1	Phthalic acid	2.0	-	-
No. 33	GL	A	C3	2.4	Phosphoric acid	0.4	-	-
No. 34		B	C4	8.7	Hydrofluoric acid	0.05	-	-
No. 35		C	C5	3.6	Hydrofluoric acid	3.0	-	-
No. 36		D	C6	0.1	Hydrofluoric acid	2.4	-	-
No. 37		E	C7	0.05	Hydrofluoric acid	6.4	Nb	1
No. 38		F	C8	3.4	Hydrofluoric acid	3.2	SiO ₂	1
No. 39		G	C9	0.8	Phosphoric acid	8.7	ZrO ₂	2.5
No. 40		H	C10	3.4	Lactic acid	9.4	TiO ₂	2.5

Table 3 Examples of Embodiment 1

	Test sheet	Composition	Metallic compound (C)		Acid (D)		(D)/Si		Colloidal dispersion (E)	
				(C)/Si						(E)/Si
No. 41	GA	A	C11	4.8	Phosphoric acid		10		Sn	3.5
No. 42		B	C12	3.9	Phosphoric acid		3.1		Hf	3.5
No. 43		C	C13	5.7	Phosphoric acid		2.8		Ce	2
No. 44		D	-	-	-		-		-	-
No. 45		E	C15	3.4	Phthalic acid		4.4		Nb	2
No. 46		F	C1	2.8	Hydrofluoric acid		6.1		SiO ₂	2.5
No. 47		G	C2	5.4	Hydrofluoric acid		3.7		ZrO ₂	2.5
No. 48		H	C3	2	Phosphoric acid		9.4		-	-
No. 49	AL	A	C4	4.8	Phosphoric acid		3.1		TiO ₂	2
No. 50		B	C5	3.6	Phosphoric acid		5.4		-	-
No. 51		C	C6	2.2	Hydrofluoric acid		9.7		Sn	3.5
No. 52		D	C7	7.8	Hydrofluoric acid		6.1		Hf	3.5
No. 53		E	C8	8.1	Tartaric acid		5.8		-	-
No. 54		F	C9	2.4	Phosphoric acid		4.4		Ce	4.5
No. 55		G	C10	3.4	Phosphoric acid		6.7		Nb	5
No. 56		H	-	-	-		-		-	-

Table 4 Evaluation of examples and comparative examples of Embodiment 1

EG		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	◎	◎	◎	◎	◎	◎
	No. 2	○	○	◎	◎	○	◎
	No. 3	◎	◎	◎	◎	◎	◎
	No. 4	◎	◎	◎	○	○	◎
	No. 5	○	○	○	◎	○	◎
	No. 6	◎	○	◎	○	○	◎
	No. 7	◎	○	◎	○	○	◎
	No. 8	◎	◎	◎	◎	◎	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		△	×	×	△	×	×
Comparative example 3		△	×	○	○	×	○
Comparative example 4		○	△	×	×	◎	○

Table 5 Evaluation of examples and comparative examples of Embodiment 1

5

GF		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 9	○	○	◎	◎	◎	◎
	No. 10	○	○	◎	○	○	◎
	No. 11	◎	○	○	○	○	◎
	No. 12	◎	◎	○	○	○	◎
	No. 13	○	○	◎	○	○	◎
	No. 14	◎	◎	◎	○	○	◎
	No. 15	◎	◎	○	◎	○	◎
	No. 16	◎	○	◎	◎	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	○	×	△	×	×
Comparative example 3		◎	○	○	○	×	○
Comparative example 4		◎	△	×	×	◎	○

Table 6 Evaluation of examples and comparative examples of Embodiment 1

ZN		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 17	○	○	○	◎	○	◎
	No. 18	○	○	○	◎	○	◎
	No. 19	◎	◎	○	○	○	◎
	No. 20	◎	○	◎	◎	◎	◎
	No. 21	○	○	○	◎	○	◎
	No. 22	◎	○	◎	◎	◎	◎
	No. 23	◎	◎	○	◎	◎	◎
	No. 24	◎	◎	◎	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	△	×	△	×	×
Comparative example 3		○	△	○	○	×	○
Comparative example 4		○	△	×	×	◎	○

Table 7 Evaluation of examples and comparative examples of Embodiment 1

5

GI		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 25	○	◎	○	◎	○	◎
	No. 26	○	○	◎	◎	◎	◎
	No. 27	○	○	○	○	○	◎
	No. 28	◎	○	◎	◎	○	◎
	No. 29	○	○	◎	◎	○	◎
	No. 30	◎	◎	◎	◎	○	◎
	No. 31	◎	◎	◎	◎	○	◎
	No. 32	◎	◎	○	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	△	×	△	×	×
Comparative example 3		○	△	○	○	×	○
Comparative example 4		◎	○	×	×	◎	○

Table 8 Evaluation of examples and comparative examples of Embodiment 1

GL		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 33	○	○	◎	○	○	◎
	No. 34	○	○	○	○	○	◎
	No. 35	◎	◎	○	○	○	◎
	No. 36	◎	◎	◎	○	○	◎
	No. 37	○	○	◎	◎	○	◎
	No. 38	◎	◎	○	◎	◎	◎
	No. 39	◎	○	◎	◎	○	◎
	No. 40	◎	○	○	◎	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		△	△	×	△	×	×
Comparative example 3		△	△	○	○	×	○
Comparative example 4		○	○	×	×	◎	○

Table 9 Evaluation of examples and comparative examples of Embodiment 1

5

GA		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 41	○	○	○	◎	○	◎
	No. 42	○	○	○	◎	○	◎
	No. 43	◎	○	○	◎	○	◎
	No. 44	○	○	○	○	○	◎
	No. 45	○	○	○	◎	◎	◎
	No. 46	◎	○	◎	◎	○	◎
	No. 47	◎	◎	○	◎	○	◎
	No. 48	◎	◎	◎	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		△	△	×	△	×	×
Comparative example 3		△	△	○	○	×	○
Comparative example 4		○	○	×	×	◎	○

Table 10 Evaluation of examples and comparative examples
of Embodiment 1

AL		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 49	○	◎	○	◎	◎	◎
	No. 50	○	○	○	○	○	◎
	No. 51	◎	◎	◎	◎	○	◎
	No. 52	◎	○	○	◎	○	◎
	No. 53	○	○	○	○	○	◎
	No. 54	◎	○	◎	◎	○	◎
	No. 55	◎	◎	○	◎	○	◎
	No. 56	○	○	○	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	◎	×	△	×	×
Comparative example 3		○	◎	○	○	×	○
Comparative example 4		◎	○	×	×	◎	○

Table 11 Examples of Embodiment 2

	Organic compound (A)	Organic compound (B)	(A):(B) (mol ratio)	Metallic compound (C)		Acid (D)	(D)/Si		Colloidal dispersion (E)	
					(C)/Si			(E)/Si		
No. 1	A1	B1	2:1	C1	0.03	Phosphoric acid	-	-	-	-
No. 2	A1	B1	2:1	C2	1.2	Phosphoric acid	0.8	ZrO ₂	1.5	1.5
No. 3	A1	B2	2:1	C3	3.7	Phosphoric acid	2.4	TiO ₂	0.2	0.2
No. 4	A1	B2	2:1	C4	5.4	Hydrofluoric acid	1.5	Sn	3.8	3.8
No. 5	A1	B5	2:1	C5	2.1	Hydrofluoric acid	3.2	Hf	2.7	2.7
No. 6	A2	B3	2:1	C6	0.01	Hydrofluoric acid	9.4	Ce	5.4	5.4
No. 7	A3	B3	2:1	C7	9.9	Hydrofluoric acid	3.1	Nb	6.8	6.8
No. 8	A4	B1	2:1	C8	8.2	Formic acid	5.4	SiO ₂	0.05	0.05
No. 9	A4	B2	2:1	C9	0.4	Butyric acid	0.04	ZrO ₂	2.4	2.4
No. 10	A4	B4	2:1	C10	6.2	Acetic acid	3.2	TiO ₂	3.9	3.9
No. 11	A5	B1	1:2	C11	8.1	Oxalic acid	4.8	Sn	2.5	2.5
No. 12	A6	B1	1:2	C12	3.4	Succinic acid	3.6	Hf	0.01	0.01
No. 13	A7	B1	1:2	C13	6.4	Lactic acid	8.7	Ce	3.3	3.3
No. 14	A8	B1	1:2	C14	2.2	Tartaric acid	6.4	Nb	7.8	7.8
No. 15	A9	B1	1:2	C15	0.1	Citric acid	3.1	SiO ₂	6.4	6.4

Table 12 Evaluation of examples and comparative examples of Embodiment 2

EG		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	◎	◎	◎	◎	◎	◎
	No. 2	○	○	◎	◎	○	◎
	No. 3	◎	◎	◎	◎	◎	◎
	No. 4	◎	◎	◎	○	○	◎
	No. 5	○	○	○	◎	○	◎
	No. 6	◎	○	◎	○	○	◎
	No. 7	◎	○	◎	○	○	◎
	No. 8	◎	◎	◎	◎	◎	◎
	No. 9	○	○	◎	◎	○	◎
	No. 10	◎	◎	◎	◎	◎	◎
	No. 11	◎	◎	◎	○	○	◎
	No. 12	○	○	○	◎	○	◎
	No. 13	◎	○	◎	○	○	◎
	No. 14	◎	○	◎	○	○	◎
	No. 15	◎	◎	◎	◎	◎	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		△	×	×	△	×	×
Comparative example 3		△	×	○	○	×	○
Comparative example 4		○	△	×	×	◎	○

Table 13 Evaluation of examples and comparative examples of Embodiment 2

GF		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	○	○	◎	◎	◎	◎
	No. 2	○	○	◎	○	○	◎
	No. 3	◎	○	○	○	○	◎
	No. 4	◎	◎	○	○	○	◎
	No. 5	○	○	◎	○	○	◎
	No. 6	◎	◎	◎	○	○	◎
	No. 7	◎	◎	○	◎	○	◎
	No. 8	◎	○	◎	◎	○	◎
	No. 9	○	○	◎	○	○	◎
	No. 10	◎	○	○	○	○	◎
	No. 11	◎	◎	○	○	○	◎
	No. 12	○	○	◎	○	○	◎
	No. 13	◎	◎	◎	○	○	◎
	No. 14	◎	◎	○	◎	○	◎
	No. 15	◎	○	◎	◎	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	○	×	△	×	×
Comparative example 3		◎	○	○	○	×	○
Comparative example 4		◎	△	×	×	◎	○

Table 14 Evaluation of examples and comparative examples of Embodiment 2

ZN		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	◎	◎	◎	◎	◎	◎
	No. 2	○	○	◎	◎	○	◎
	No. 3	◎	◎	◎	◎	◎	◎
	No. 4	◎	◎	◎	○	○	◎
	No. 5	○	○	○	◎	○	◎
	No. 6	◎	○	◎	○	○	◎
	No. 7	◎	○	◎	○	○	◎
	No. 8	◎	◎	◎	◎	◎	◎
	No. 9	○	○	◎	◎	○	◎
	No. 10	◎	◎	◎	◎	◎	◎
	No. 11	◎	◎	◎	○	○	◎
	No. 12	○	○	○	◎	○	◎
	No. 13	◎	○	◎	○	○	◎
	No. 14	◎	○	◎	○	○	◎
	No. 15	◎	◎	◎	◎	◎	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		△	×	×	△	×	×
Comparative example 3		△	×	○	○	×	○
Comparative example 4		○	△	×	×	◎	○

Table 15 Evaluation of examples and comparative examples of Embodiment 2

GI		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	○	○	◎	◎	◎	◎
	No. 2	○	○	◎	○	○	◎
	No. 3	◎	○	○	○	○	◎
	No. 4	◎	◎	○	○	○	◎
	No. 5	○	○	◎	○	○	◎
	No. 6	◎	◎	◎	○	○	◎
	No. 7	◎	◎	○	◎	○	◎
	No. 8	◎	○	◎	◎	○	◎
	No. 9	○	○	◎	○	○	◎
	No. 10	◎	○	○	○	○	◎
	No. 11	◎	◎	○	○	○	◎
	No. 12	○	○	◎	○	○	◎
	No. 13	◎	◎	◎	○	○	◎
	No. 14	◎	◎	○	◎	○	◎
	No. 15	◎	○	◎	◎	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	○	×	△	×	×
Comparative example 3		◎	○	○	○	×	○
Comparative example 4		◎	△	×	×	◎	○

Table 16 Evaluation of examples and comparative examples of Embodiment 2

GL		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	○	○	○	◎	○	◎
	No. 2	○	○	○	◎	○	◎
	No. 3	◎	◎	○	○	○	◎
	No. 4	◎	○	◎	◎	◎	◎
	No. 5	○	○	○	◎	○	◎
	No. 6	◎	○	◎	◎	◎	◎
	No. 7	◎	◎	○	◎	◎	◎
	No. 8	◎	◎	◎	○	○	◎
	No. 9	○	○	○	◎	○	◎
	No. 10	◎	◎	○	○	○	◎
	No. 11	◎	○	◎	◎	◎	◎
	No. 12	○	○	○	◎	○	◎
	No. 13	◎	○	◎	◎	◎	◎
	No. 14	◎	◎	○	◎	◎	◎
	No. 15	◎	◎	◎	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	△	×	△	×	×
Comparative example 3		○	△	○	○	×	○
Comparative example 4		○	△	×	×	◎	○

Table 17 Evaluation of examples and comparative examples of Embodiment 2

GA		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	○	◎	○	◎	○	◎
	No. 2	○	○	◎	◎	◎	◎
	No. 3	○	○	○	○	○	◎
	No. 4	◎	○	◎	◎	○	◎
	No. 5	○	○	◎	◎	○	◎
	No. 6	◎	◎	◎	◎	○	◎
	No. 7	◎	◎	◎	◎	○	◎
	No. 8	◎	◎	○	○	○	◎
	No. 9	○	○	◎	◎	◎	◎
	No. 10	○	○	○	○	○	◎
	No. 11	◎	○	◎	◎	○	◎
	No. 12	○	○	◎	◎	○	◎
	No. 13	◎	◎	◎	◎	○	◎
	No. 14	◎	◎	◎	◎	○	◎
	No. 15	◎	◎	○	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	△	×	△	×	×
Comparative example 3		○	△	○	○	×	○
Comparative example 4		◎	○	×	×	◎	○

Table 18 Evaluation of examples and comparative examples
of Embodiment 2

AI		Corrosion resistance		Electric conductivity	Heat resistance	Finger-print resistance	Stability
		Plane part	Wrought part				
Example	No. 1	○	◎	○	◎	◎	◎
	No. 2	○	○	○	○	○	◎
	No. 3	◎	◎	◎	◎	○	◎
	No. 4	◎	○	○	◎	○	◎
	No. 5	○	○	○	○	○	◎
	No. 6	◎	○	◎	◎	○	◎
	No. 7	◎	◎	○	◎	○	◎
	No. 8	○	○	○	○	○	◎
	No. 9	○	○	○	○	○	◎
	No. 10	◎	◎	◎	◎	○	◎
	No. 11	◎	○	○	◎	○	◎
	No. 12	○	○	○	○	○	◎
	No. 13	◎	○	◎	◎	○	◎
	No. 14	◎	◎	○	◎	○	◎
	No. 15	○	○	○	○	○	◎
Comparative example 1		○	○	◎	×	○	△
Comparative example 2		○	◎	×	△	×	×
Comparative example 3		○	◎	○	○	×	○
Comparative example 4		◎	○	×	×	◎	○

CLAIMS

1. An aqueous metal surface-treating agent wherein an organic silicon compound which has, in one molecule, two or more of functional groups (a) represented by the
5 formula $-\text{SiR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 represent mutually independently alkyl groups, alkoxyl groups or hydroxyl groups, and at least one of them is an alkoxyl group) and at least one hydrophilic functional group (b) selected
10 from hydroxyl groups (which are different from those containable in the functional groups (a)), amino groups, carboxyl groups, phosphoric acid groups, phosphonic acid groups, sulfonic acid groups, polyoxyethylene chains and amido groups, and has a molecular weight, per one functional group (b), of 100 to 10,000, is compounded.

15 2. An aqueous metal surface-treating agent wherein an organic compound (A) having a functional group (I), and an organic compound (B) having a functional group (II) capable of reacting with the functional group (I) and at least one hydrophilic functional
20 group (III) selected from hydroxyl groups (which are different from those containable in the following functional groups (a)), primary, secondary and tertiary amino groups, quaternary ammonium groups, phosphoric acid groups, phosphonic acid groups, sulfonic acid groups,
25 primary amido groups, secondary amido groups and polyoxyethylene chains, all these groups and chains being different from those included in the functional groups (I) and/or the functional groups (II) are compounded, and at least one of the organic compound (A) and the organic compound (B) is an organic silane
30 compound having a functional group (a) represented by the formula $-\text{SiR}^1\text{R}^2\text{R}^3$ (wherein R^1 , R^2 and R^3 are as defined above).

3. The surface-treating agent according to claim 2 wherein each of the functional group (I) and the functional group (II) is, mutually independently, at least one functional group selected from hydroxyl groups (which are different from those containable in the functional groups (a)), glycidyl groups, primary amino groups, secondary amino groups, mercapto groups, isocyanato groups, carboxyl groups, methylol groups, active methylene groups, imido groups, amido groups, carbonyl groups and vinyl groups.

4. The surface-treating agent according to any one of claims 1 to 3 wherein a metallic compound (C) containing a bivalent or more metallic ion (when the metallic ion is a Zr ion, a Ti ion, a Hf ion or a Ce ion, the case where the metallic compound (C) is a colloidal dispersoid is excluded) is compounded.

5. The surface-treating agent according to any one of claims 1 to 4 wherein the bivalent or more metallic ion is at least one selected from Ti, Zr, Hf, V, Mg, Mn, Zn, W, Mo, Al, Ni, Co, Ce and Ca ions.

6. The surface-treating agent according to claim 4 or 5 wherein the mass ratio of the content of the metallic compound (C) to the content of Si derived from the functional group (a), in a coat obtained from the surface-treating agent, (C)/Si, is 0.01 to 10.0.

7. The surface-treating agent according to any one of claims 1 to 6 wherein a product formed by the reaction of the organic silicon compounds themselves or the reaction of the organic compound (A) with the organic compound (B) has at least one sioxane bond formed by condensation of two or more functional groups (a).

8. The surface-treating agent according to any one of claims 1 to 7 wherein at least one acid (D) selected

from hydrofluoric acid, organic acids and phosphoric acid is compounded.

5 9. The surface-treating agent according to claim 8 wherein the mass ratio of the content of the acid (D) to the content of Si derived from the functional group (a), in a coat obtained from the surface-treating agent, (D)/Si, is 0.01 to 10.0.

10 10. The surface-treating agent according to any one of claims 1 to 9 wherein a colloidal dispersion (E) of the simple substance or compound of at least one element selected from Si, Zr, Ti, Sn, Hf, Ce and Nb is compounded.

15 11. A process for surface-treating a metallic material which comprises applying the surface-treating agent according to any one of claims 1 to 10 onto the surface of the metallic material, and drying the resulting surface-treating agent to form a coating of 10 to 3,000 mg/m² in terms of SiO₂.

20 12. A metallic material surface-treated by the process according to claim 11.