

SPECIFICATION

5 SURFACE TREATMENT LIQUID FOR ZINC OR ZINC ALLOY PLATED STEEL SHEET, ZINC OR ZINC ALLOY PLATED STEEL SHEET, AND METHOD OF PRODUCING THE STEEL SHEET

Technical Field

[0001] The present invention relates to a galvanized steel sheet suitably used for applications requiring good oil retaining properties in a high-temperature environment or
10 a high-temperature and high-humidity environment such as motor cases (motor cases including bearing holder portions for holding bearings) of various types, and a method of producing the galvanized steel sheet. The present invention also relates to a surface treatment liquid useful for achieving good oil retaining properties in a high-temperature environment or a high-temperature and high-humidity environment.

15 Prior Art

[0002] At present there are widely used such bearings as each produced by forming anti-rust coating on a surface of a zinc or zinc alloy plated steel sheet and subjecting the steel sheet to deformation processing, for bearings in motor cases of various motors for use in automobiles, AV (audio-visual) and OA (office automation) devices, and the like.
20 These bearings are roughly classified into a rolling-element bearing and a sliding bearing. In recent years, motors as electrical components of automobiles, as well as various motors of electronic recording devices such as HDD and electronic apparatuses such as photocopying machine and the like, predominantly use sliding bearings as bearings thereof.

[0003] In a sliding bearing, lubricating oil is supplied to a bearing portion, so that a hydraulic pressure is generated by the lubricating oil when a rotating shaft is rotated and thus the rotating shaft is prevented from having contact with or adhesion to the bearing by the action of the hydraulic pressure. Further, vibrations and noises of motors can be prevented from occurring by the action of the lubricating oil.

[0004] In general, bearings (bearing members) of various motors for use in automobiles, OA and AV devices have structures in which the bearings are held and fixed by bearing holder portions formed in motor cases. In order to prevent lubricating oil from oozing in such a bearing portion of a motor as described above, researchers have conventionally

paid their attention mainly to improvement of bearing materials, structures of bearing portions and vicinities thereof, and the like.

For example, JP-A 07-238934 and JP-A 09-210065 each disclose a method of preventing lubricating oil from oozing from a bearing portion by improving a bearing material, structures of the bearing portion and vicinities thereof and the like. However, simply improving bearing structures as described above cannot cause a sufficient oozing preventing effect.

[0004] There are widely used such motor cases as each produced by forming anti-rust coating on a surface of a zinc or zinc alloy plated steel sheet and subjecting the steel sheet to deformation processing. When lubricating oil oozes from a bearing portion made of a bearing material, the lubricating oil starts oozing and spreads from the bearing portion (the bearing material) to the inner surface of a motor case in the vicinities of a bearing holder portion. As a result, lubricity of the bearing portion is rendered insufficient, whereby a rotating shaft is more likely to have contact with or adhesion to the bearing and vibrations and noises of a motor are resulted therefrom.

JP-A 2009-035758 and JP-A 2008-169470 each propose a surface-treated zinc or zinc alloy plated steel sheet excellent in corrosion resistance, blackening resistance, and appearance and corrosion resistance after press molding. However, these steel sheets can hardly cause any oil retaining effect and, if they can cause some oil retaining effect at the room temperature, the effect is decreased to a quite limited one in a harsh environment such as a high-temperature environment or a high-temperature and high-humidity environment.

JP-A 2009-287049 proposes a film containing an organopolysiloxane compound as a silicon compound and JP-A 2010-070786 proposes a film containing an organopolysiloxane compound as an essential component of a silicon compound. However, neither JP-A 2009-287049 nor JP-A 2010-070786 aims at improving oil retaining properties of a steel sheet.

Disclosure of the Invention

[0005] Problems to be solved by the Invention

[0006] The present invention has been contrived in view of the situations described above, and one object thereof is to provide a zinc or zinc alloy plated steel sheet and a method of the same, which zinc or zinc alloy plated steel sheet is of course excellent in appearance and corrosion resistance after press molding and also excellent in oil

retaining properties in a high-temperature environment or a high-temperature and high-humidity environment and capable of effectively preventing oozing of lubricating oil (which would result in shortage of lubricating oil in a bearing) from occurring in a case, in particular, where the steel sheet is applied to a member such as a motor case having a bearing holder portion for holding a bearing.

Further, another object of the present invention is to provide a surface treatment liquid suitable for obtaining a surface-treated film which is excellent in oil retaining properties in a high-temperature environment or a high-temperature and high-humidity environment.

10 Means for solving the Problem

[0007] As a result of a keen study to solve the aforementioned problems, the inventors of the present invention have newly discovered that lubricating oil oozes from a bearing portion mainly because the inner surface of a motor case including a bearing holder portion (i.e. the inner surface of a surface-treated steel sheet) exhibits wettability to lubricating oil and that the lubricating oil in the bearing portion continually oozes onto the inner surface of the motor case in the vicinities of the bearing portion, wets and spreads on the inner surface due to this surface property or wettability of the inner surface.

The inventors have also discovered, as a solution for the aforementioned problem, that: the lubricating oil can be sealed within the bearing by suppressing spread-out of the lubricating oil from the bearing onto the inner surface of the motor case by making the inner surface of a motor case including a bearing holder portion (i.e. the inner surface of a surface-treated steel sheet) exhibit relatively low wettability; and oozing of lubricating oil (which would result in shortage of lubricating oil in a bearing) can be effectively prevented from occurring, accordingly.

Further, the inventors have discovered that a surface-treated steel sheet, produced by: coating a surface of a zinc or zinc alloy plated steel sheet with a surface treatment liquid as a water-soluble zirconium compound based solution containing a predetermined content of organopolysiloxane compound; and drying the steel sheet thus coated, is very useful to achieve the objects describe above, thereby completing the present invention.

[0008] Specifically, main features of the present invention are as follows.

1. A surface treatment liquid for a zinc or zinc alloy plated steel sheet, comprising in conditions satisfying (1) to (8) below:

- (A) a water-soluble zirconium compound;
(B) a water-dispersible silica fine particles;
(C) a silane coupling agent;
(D) a vanadic acid compound;
5 (E) a phosphoric acid compound;
(F) a nickel compound;
(G) an acrylic resin emulsion; and
(H) an organopolysiloxane compound,
wherein: (1) a mass ratio $(B_S)/(A_{Zr})$ of mass of a solid content (B_S) of the water-
10 dispersible silica fine particles (B) with respect to mass (A_{Zr}) in terms of zirconium
standard of the water-soluble zirconium compound (A) is in the range of 0.3 to 1.2;
(2) a mass ratio $(C)/(A_{Zr})$ of mass of a silane coupling agent (C) with respect to
mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A)
is in the range of 0.6 to 2.5;
15 (3) a mass ratio $(D_V)/(A_{Zr})$ of mass (D_V) in terms of vanadium standard of the
vanadic acid compound (D) with respect to mass (A_{Zr}) in terms of zirconium standard of
the water-soluble zirconium compound (A) is in the range of 0.04 to 0.15;
(4) a mass ratio $(E_P)/(A_{Zr})$ of mass (E_P) in terms of phosphorus standard of the
phosphoric acid compound (E) with respect to mass (A_{Zr}) in terms of zirconium standard
20 of the water-soluble zirconium compound (A) is in the range of 0.11 to 0.55;
(5) a mass ratio $(F_{Ni})/(A_{Zr})$ of mass (F_{Ni}) in terms of nickel standard of the nickel
compound (F) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-
soluble zirconium compound (A) is in the range of 0.015 to 0.065;
(6) a proportion of solid content (G_S) of the acrylic resin emulsion (G) in the total
25 solid contents of the surface treatment liquid is in the range of 0.5 to 10 mass %;
(7) a proportion of solid content (H_S) of the organopolysiloxane compound (H) in
the total solid contents of the surface treatment liquid is in the range of 0.55 to 6.5
mass %; and
(8) a mass ratio $(Si_T)/(A_{Zr})$ of the total mass (Si_T) in terms of silicon standard of
30 the water-dispersible silica fine particles (B), the silane coupling agent (C) and the
organopolysiloxane compound (H) with respect to mass (A_{Zr}) in terms of zirconium
standard of the water-soluble zirconium compound (A) is in the range of 0.23 to 1.0.

[0009] 2. The surface treatment liquid for a zinc or zinc alloy plated steel sheet of

(1) above, further comprising a wax (I) in a condition satisfying (9) below,

wherein (9) a proportion of solid content (I_s) of the wax (I) in the total solid contents of the surface treatment liquid is in the range of 2.5 to 10 mass %.

[0010] 3. A method of producing a surface-treated zinc or zinc alloy plated steel sheet, comprising:

coating a surface of a zinc or zinc alloy plated steel sheet with the surface treatment liquid of (1) or (2) above; and

drying the zinc or zinc alloy plated steel sheet thus coated by heating,

wherein a film coating quantity in terms of zirconium content per one surface is in the range of 10 to 200 mg/m^2 .

[0011] 4. A zinc or zinc alloy plated steel sheet having a film formed on a surface thereof, the film comprising in conditions satisfying (11) to (15) below:

(a) a zirconium compound;

(b) silica fine particles;

(c) a component derived from a silane coupling agent;

(d) a vanadic acid compound;

(e) a phosphoric acid compound;

(f) a nickel compound;

(g) an acrylic resin; and

(h) a component derived from an organopolysiloxane compound,

wherein: (11) a mass ratio (d_v)/(a_{Zr}) of mass (d_v) in terms of vanadium standard of the vanadic acid compound (d) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.04 to 0.15;

(12) a mass ratio (e_p)/(a_{Zr}) of mass (e_p) in terms of phosphorus standard of the phosphoric acid compound (e) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.11 to 0.55;

(13) a mass ratio (f_{Ni})/(a_{Zr}) of mass (f_{Ni}) in terms of nickel standard of the nickel compound (f) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.015 to 0.065;

(14) a proportion in weight of the acrylic resin (g) in the total solid contents of the film is in the range of 0.5 to 10 mass %;

(15) a mass ratio (Si_t)/(a_{Zr}) of the total mass (Si_t) in terms of silicon standard of the silica fine particles (b), the component derived from the silane coupling agent (c) and the

component derived from the organopolysiloxane compound (h) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.23 to 1.0; and

5 a film coating quantity in terms of zirconium content per one surface is in the range of 10 to 200 mg/m².

[0012] 5. The zinc or zinc alloy plated steel sheet of (4) above, where the film further comprises a wax (i) in a condition satisfying (16) below,

wherein (16) a proportion of solid content (i_s) of the wax (i) in the total solid contents of the film is in the range of 2.5 to 10 mass %.

10 Effect of the Invention

[0013] According to the present invention, there can be obtained a zinc or zinc alloy plated steel sheet excellent in not only appearance and corrosion resistance after press molding but also oil retaining properties in a high-temperature environment or a high-temperature and high-humidity environment.

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Best Mode for carrying out the Invention

[0014] The present invention will be described in detail hereinafter.

Any steel sheet having a plate film containing zinc is acceptable without particular restriction to the type thereof as a zinc or zinc alloy plated steel sheet for use in a base
20 material of a surface-treated steel sheet of the present invention. Examples of the acceptable steel sheet include: a zinc plated steel sheet such as a hot dip galvanized steel sheet (GI) or a galva-annealed steel sheet (GA) obtained by alloying of a hot dip galvanized steel sheet; a Zn-Ni plated steel sheet; a Zn-Al alloy plated steel sheet (e.g. a Zn-5 mass% Al alloy plated steel sheet, a Zn-55 mass% Al alloy plated steel sheet); and
25 a Zn-Al-Mg plated steel sheet (e.g. a Zn-6 mass% Al-3 mass% Mg alloy plated steel sheet, a Zn-11 mass% Al-3 mass% Mg alloy plated steel sheet); and the like.

[0015] Examples which can be used, of a zinc or zinc alloy plated steel sheet as a base material of the surface-treated steel sheet, further include: a plated steel sheet similar to the zinc or zinc alloy plated steel sheets described above and of which plating
30 layer further contains, as small amounts of metal elements of different types or impurities, at least one of nickel, cobalt, manganese, iron, molybdenum, tungsten, titanium, chromium, aluminum, magnesium, lead, antimony, tin, and copper; and a multilayer-plated steel sheet having two or more plating layers of the same type or

different types selected from the aforementioned plating layers.

[0016] Next, a surface treatment liquid for the zinc or zinc alloy plated steel sheet of the present invention will be described.

The surface treatment liquid of the present invention contains in water as a solvent: (A) a
5 water-soluble zirconium compound; (B) a water-dispersible silica fine particles; (C) a silane coupling agent; (D) a vanadic acid compound; (E) a phosphoric acid compound; and (F) a nickel compound; (G) an acrylic resin emulsion; (H) an organopolysiloxane compound; and optionally (I) a wax.

[0017] Among the film components described above, the water-soluble zirconium
10 compound is a component for forming skeleton of the film and causes an effect of improving corrosion resistance and ensuring good appearance after press molding. Examples of the water-soluble zirconium compound (A) include zirconium nitrate, zirconium oxynitrate, zirconium acetate, zirconium sulfate, ammonium zirconium carbonate, potassium zirconium carbonate, sodium zirconium carbonate and the like.
15 These compounds may be used either solely or in combination of two or more types. Examples of the water-soluble zirconium compound (A) further include an inorganic fluoride-containing compound such as hexafluorozirconic acid and a salt thereof as long as the compound is compatible with the surface treatment liquid.

[0018] Among the film components described above, the water-dispersible silica
20 fine particles cause as a main effect an effect of improving corrosion resistance and ensuring good appearance after press molding, of the resulting film. Examples of the water-dispersible silica fine particles (B) include colloidal silica and dry silica without particular limitation to particle diameter, types and the like thereof. Examples of colloidal silica include SNOWTEX O, C, N, 20, OS, OXS ® manufactured
25 by Nissan Chemical Industries, Ltd. and examples of dry silica include AEROSIL 50, 130, 200, 300, 380 ®. These compounds may be used either solely or in combination of two or more types.

[0019] Regarding a blending ratio of the water-dispersible silica fine particles (B), a
mass ratio $(B_s)/(A_{Zr})$ of mass of a solid content (B_s) of the water-dispersible silica fine
30 particles (B) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is set in the range of 0.3 to 1.2. In a case where the ratio $(B_s)/(A_{Zr})$ is smaller than 0.3, corrosion resistance and appearance after press molding of the steel sheet deteriorate. In a case where the ratio $(B_s)/(A_{Zr})$ exceeds 1.2, a

film formation is disturbed and corrosion resistance of the steel sheet deteriorates. The ratio $(B_s)/(A_{Zr})$ is preferably in the range of 0.4 to 0.9.

[0020] The silane coupling agent (C) among the aforementioned film components is crosslinking-reacted with the water-soluble zirconium compound (A) and the water-dispersible silica fine particles (B), respectively, to form a film having a three-dimensional crosslinked reaction structure. As a result, the silane coupling agent (C) causes an effect of improving corrosion resistance, oil-retaining properties and the like of the film thus obtained. The silane coupling agent (C) makes particular contribution to production of a film having excellent corrosion resistance, which corrosion resistance cannot be obtained by using the water-soluble zirconium compound (A) and the water-dispersible silica fine particles (B) only.

Examples of the silane coupling agent (C) include vinylmethoxysilane, vinylethoxysilane, vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, γ -glycidoxypropyltriethoxysilane, N- β (aminoethyl) γ -aminopropylmethyldimethoxysilane, N- β (aminoethyl) γ -aminopropylmethyldimethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, p-styryltrimethoxysilane, γ -acryloxypropyltrimethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, γ -ureidopropyltriethoxysilane, γ -chloropropyltrimethoxysilane, bis(triethoxysilylpropyl)tetrasulfide, γ -isocyanatepropyltriethoxysilane, γ -triethoxysilyl-N-(1,3-dimethyl-butylidene)propylamine, N-(vinylbenzylamine)- β -aminoethyl- γ -aminopropyltrimethoxysilane, and the like. These compounds may be used either solely or in combination of two or more types.

[0021] Regarding a blending ratio of the silane coupling agent (C), a mass ratio $(C)/(A_{Zr})$ of mass of the silane coupling agent (C) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is set in the range of 0.6 to 2.5. In a case where the ratio $(C)/(A_{Zr})$ is smaller than 0.6, appearance after press molding and oil-retaining properties of the steel sheet deteriorate. In a case where the ratio $(C)/(A_{Zr})$ exceeds 2.5, a film formation is disturbed and corrosion resistance of the

steel sheet and stability of the surface treatment liquid deteriorate. The ratio $(C)/(A_{Zr})$ is preferably in the range of 0.8 to 1.8. In the present embodiment, the silane coupling agent (C) contains solid content by 100%.

[0022] The vanadic acid compound among the aforementioned film components is reacted with the phosphoric acid compound described below to form a salt having poor solubility, thereby fixing the phosphoric acid compound in the film and effectively improving corrosion resistance of the film.

In the present embodiment, examples of the vanadic acid compound (D) include ammonium metavanadate and sodium metavanadate. These compounds may be used either solely or in combination of two or more types.

[0023] Regarding a blending ratio of the vanadic acid compound (D), a mass ratio $(D_V)/(A_{Zr})$ of mass (D_V) in terms of vanadium standard of the vanadic acid compound (D) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is set in the range of 0.04 to 0.15. In a case where the ratio $(D_V)/(A_{Zr})$ is smaller than 0.04, corrosion resistance of the steel sheet deteriorates. In a case where the ratio $(D_V)/(A_{Zr})$ exceeds 0.15, appearance of the steel sheet after press molding deteriorates. The ratio $(D_V)/(A_{Zr})$ is preferably in the range of 0.06 to 0.14.

[0024] The phosphoric acid compound among the aforementioned film components is reacted with the plating film of the zinc or zinc alloy plated steel sheet as the base material and forms a salt having poor solubility, thereby being an effective component in terms of improving corrosion resistance of the film.

In the present embodiment, types of the phosphoric acid compound (E) is not particularly restricted as long as the phosphoric acid compound (E) is compatible with the surface treatment liquid and examples of the water-soluble phosphoric acid compound include: phosphoric acid; primary phosphate; secondary phosphate; orthophosphate ; condensed phosphoric acid and/or condensed phosphate such as pyrophosphoric acid, pyrophosphate, tripolyphosphoric acid and tripolyphosphate; phosphorus acid; phosphite; hypophosphoric acid; hypophosphite; phosphonic acid; phosphonate; and the like.

Examples of phosphonic acid salt include nitylotris(methylene)phosphonic acid, phosphonobutane tricarboxylic acid, ethylenediaminetetramethylene phosphonic acid, methyldiphosphonic acid, methylenephosphonic acid, ethylenediphosphonic acid, 1-hydroxymethane-1,1-diphosphonic acid, and ammonium salt, alkali metal salt thereof

and the like. These phosphoric acid compounds may be used either solely or in combination of two or more types.

[0025] Regarding a blending ratio of the phosphoric acid compound (E), a mass ratio $(E_P)/(A_{Zr})$ of mass (E_P) in terms of phosphorus standard of the phosphoric acid compound (E) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.11 to 0.55. In a case where the ratio $(E_P)/(A_{Zr})$ is smaller than 0.11, corrosion resistance of the steel sheet deteriorates. In a case where the ratio $(E_P)/(A_{Zr})$ exceeds 0.55, appearance of the steel sheet after press molding deteriorates. The ratio $(E_P)/(A_{Zr})$ is preferably in the range of 0.20 to 0.37.

[0026] The nickel compound among the aforementioned film components is substitution-deposited on the plating film of the zinc or zinc alloy plated steel sheet as the base material and forms a salt having poor solubility, thereby being an effective component in terms of improving corrosion resistance of the film.

In the present embodiment, types of the nickel compound (F) is not particularly restricted as long as the nickel compound (F) is compatible with the surface treatment liquid and examples of the nickel compound (F) include nickel nitrate, nickel sulfate, nickel carbonate, nickel chloride, nickel phosphate, and the like. These nickel compounds may be used either solely or in combination of two or more types.

[0027] Regarding a blending ratio of the nickel compound (F), a mass ratio $(F_{Ni})/(A_{Zr})$ of mass (F_{Ni}) in terms of nickel standard of the nickel compound (F) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.015 to 0.065. In a case where the ratio $(F_{Ni})/(A_{Zr})$ is smaller than 0.015 or exceeds 0.065, corrosion resistance of the steel sheet deteriorates. The ratio $(F_{Ni})/(A_{Zr})$ is preferably in the range of 0.023 to 0.049.

[0028] The acrylic resin emulsion among the aforementioned film components forms skeleton of the film and therefore is an effective component in terms of improving corrosion resistance of the film.

Examples of the acrylic resin emulsion (G) include water-based emulsion resins obtained by emulsion polymerization of vinyl monomers such as acrylic acid, methacrylic acid, acrylic acid ester, methacrylic acid ester, styrene and the like. Presence/absence of an emulsifier and types of the emulsifier are, however, not particularly restricted as long as the acrylic resin emulsion (G) is compatible with the surface treatment liquid. Non-ionic emulsifiers are especially suitable for use. Non-ionic emulsifiers having polyethylene

oxide and/or polypropylene oxide in the structure thereof are the most suitable for use among the non-ionic emulsifiers.

[0029] Regarding a blending ratio of solid content (G_S) of the acrylic resin emulsion (G), a proportion of the solid content (G_S) of the acrylic resin emulsion (G) in the total solid contents of the surface treatment liquid is set in the range of 0.5 to 10 mass %. In a case where the proportion is less than 0.5 mass %, corrosion resistance of the steel sheet deteriorates. In a case where the proportion exceeds 10 mass %, appearance of the steel sheet after press molding deteriorates due to increase in content of organic components. The proportion is preferably in the range of 1 to 9 mass % and more preferably in the range of 2 to 8 mass %.

[0030] Regarding the non-ionic acrylic resin emulsion, it is preferable to use one having the glass transition temperature (T_g) calculated by formula (1) below (generally referred to as “Fox equation”) in the range of 10 to 30 °C

$$1/T_g = \Sigma (W_i/T_{gi}) \quad \cdots (1)$$

In formula (1), W_i represents a mass fraction of the component (i) and T_{gi} represents T_g (K) of the component (i).

By using a non-ionic acrylic resin emulsion of which T_g is 10 °C or higher, deterioration in appearance of the steel sheet after press molding can be avoided. By using a non-ionic acrylic resin emulsion of which T_g is 30 °C or lower, deterioration in corrosion resistance of the steel sheet can be avoided.

[0031] In the present invention, an organopolysiloxane compound plays an important role to achieve the main object thereof, i.e. to realize good oil-retaining properties in a high-temperature environment or a high-temperature and high-humidity environment.

In the present embodiment, types of the organopolysiloxane compound (H) are not particularly limited as long as the compound can be blended with the surface treatment liquid. An organopolysiloxane compound can be used after being subjected to mechanical emulsion and/or emulsion polymerization by an appropriate emulsifier.

Specific examples of the organopolysiloxane compound (H) include: alkoxysilane such as methyltrimethoxysilane, methyltriethoxysilane, methyltripropoxysilane, methyltributoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, propyltrimethoxysilane, propyltriethoxysilane, butyltrimethoxysilane, pentyltrimethoxysilane, hexyltrimethoxysilane, octyltrimethoxysilane,

decyltrimethoxysilane, dodecyltrimethoxysilane, tetradecyltrimethoxysilane, octadecyltrimethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane; and silicone
5 oils such as methylhydrogen silicone oil, dimethyl silicone oil, diethyl silicone oil, diisopropyl silicone oil, dibutyl silicone oil, diamyl silicone oil, dihexyl silicone oil, dilauryl silicone oil, distearyl silicone oil, methylphenyl silicon oil, diphenyl silicon oil, ethylphenyl silicon oil, isopropylphenyl silicon oil, butylphenyl silicon oil, amylphenyl silicon oil, hexylphenyl silicon oil, laurylphenyl silicon oil, stearylphenyl silicon oil; and
10 the like.

In the present embodiment, these compounds may be used either solely or in combination of two or more types.

[0032] An organopolysiloxane compound exhibiting viscosity in the range of 1 to 100,000 mm²/s at 25°C is especially suitable among these examples. By using an
15 organopolysiloxane compound of which viscosity at 25°C is 1 mm²/s or higher, good oil-retaining properties of the steel sheet is ensured. By using an organopolysiloxane compound of which viscosity at 25°C is 100,000 mm²/s or lower, good compatibility of the compound with the surface treatment liquid is ensured.

[0033] Regarding a blending ratio of solid content (H_S) of the organopolysiloxane compound (H), a proportion of solid content (H_S) of the organopolysiloxane compound (H) in the total solid contents of the surface treatment liquid is set in the range of 0.55 to 6.5 mass %. In a case where the proportion is less than 0.55 mass %, oil-retaining
20 properties of the steel sheet deteriorates. In a case where the proportion exceeds 6.5 mass %, the effect of improving oil-retaining properties reaches the plateau, while corrosion resistance of the steel sheet starts to deteriorate. The proportion is preferably in
25 the range of 0.7 to 4.6 mass %.

[0034] A mass ratio (Si_T)/(A_{Zr}) of the total mass (Si_T) in terms of silicon standard of the water-dispersible silica fine particles (B), the silane coupling agent (C) and the organopolysiloxane compound (H) with respect to mass (A_{Zr}) in terms of zirconium
30 standard of the water-soluble zirconium compound (A) is set in the range of 0.23 to 1.0. In a case where the ratio (Si_T)/(A_{Zr}) is smaller than 0.23, corrosion resistance and appearance after press molding of the steel sheet deteriorate. In a case where the ratio (Si_T)/(A_{Zr}) exceeds 1.0, corrosion resistance of the steel sheet deteriorates. The ratio

(Si_T)/(A_{Zr}) is preferably in the range of 0.30 to 0.67.

[0035] In the present invention, the surface treatment liquid may further contain a wax (I) for improving corrosion resistance after press molding of the steel sheet.

Types of the wax (I) is not particularly restricted as long as the wax (I) is compatible
5 with the surface treatment liquid.

Examples of the wax (I) include polyolefin wax such as polyethylene, montan wax, paraffin wax, microcrystalline wax, carnauba wax, lanolin wax, and fluorinated wax. These waxes may be used either solely or in combination of two or more types.

[0036] When the surface treatment liquid contains the wax (I), a proportion of solid
10 content (I_S) of the blended wax (I) in the total solid contents of the surface treatment liquid is preferably set in the range of 2.5 to 10 mass %. In a case where the proportion is 2.5 mass % or higher, appearance of the steel sheet after press molding is prevented from deteriorating. In a case where the proportion is 10 mass % or lower, corrosion resistance of the steel sheet is prevented from deteriorating. The proportion is preferably in the
15 range of 3.4 to 7.1 mass %.

[0037] The pH value of the surface treatment liquid of the present invention, although it is not particularly restricted, is preferably in the range of pH 6 to 11 in terms of keeping the surface treatment liquid in a stable condition. By setting pH of the surface treating liquid at 6 or higher, the surface treatment liquid remains stable and corrosion
20 resistance thereof does not deteriorate. By setting pH of the surface treating liquid at 11 or lower, zinc in the plating film of the base material is appropriately etched and corrosion resistance of the steel sheet does not deteriorate. The pH value of the surface treatment liquid is more preferably in the range of pH 8 to 10.

Preferable examples of alkali to be used for adjusting the pH value of the surface
25 treatment liquid include ammonia and amine. On the other hand, a phosphoric compound is preferably used as an acid for adjusting the pH value of the surface treatment liquid.

[0038] A concentration of the surface treatment liquid of the present invention is not particularly restricted unless the concentration adversely affects coating properties of
30 the surface treatment liquid in application thereof onto a zinc or zinc alloy plated steel sheet and formation of a Zr-containing treatment film on the zinc or zinc alloy plated steel sheet. The concentration of the surface treatment liquid (as solid content) is preferably in the range of 1 to 20 mass % with respect to water as a solvent.

[0039] A surface treatment film is formed by coating the aforementioned surface treatment liquid on a surface of a zinc or zinc alloy plated steel sheet and drying the steel sheet thus coated by heating. It is critically important that a coating quantity of the surface treatment film after being dried by heating is adjusted such that the content of the zirconium compound in the surface treatment film in terms of zirconium standard (this specific Zr content will be referred to as a “film coating quantity (Zr)” hereinafter) is within the range of 10 to 200 mg/m². In a case where the “film coating quantity (Zr)” is less than 10 mg/m², corrosion resistance and oil-retaining properties at a high-temperature environment of the steel sheet cannot be obtained in a satisfactory manner.

5

10 In a case where the “film coating quantity (Zr)” exceeds 200 mg/m², the film is so thick that appearance after press molding and corrosion resistance of the steel sheet both deteriorate. The “film coating quantity (Zr)” is preferably in the range of 30 to 150 mg/m².

It is acceptable to apply the surface treatment liquid on a zinc or zinc alloy plated steel sheet by not single coating but plural coatings.

15

[0040] A conventional known method can be used in formation of a surface treatment film by coating a zinc or zinc alloy plated steel sheet with the surface treatment liquid and drying the steel sheet thus coated by heating.

Examples of a coating method include roll coating (three roll type, two roll type), squeeze coating, and whatever which is appropriate. Coating may be carried out by coating treatment by a squeeze coater or the like, immersion treatment, or spray treatment. It is acceptable to adjust the coating quantity, make the appearance of the coating and the film thickness uniform by using an air knife or a squeeze roller thereafter.

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[0041] Examples of a heating means for drying a coated steel sheet by heating include, without any particular restriction, a dryer, an air heating furnace, a high frequency induction heating furnace, an infrared furnace, and the like. The temperature (the peak metal temperature) during the heating process for drying is preferably set in the range of 50 to 250 °C. In a case where the peak metal temperature is not higher than 250 °C, cracks are not generated in the surface treatment film and thus corrosion resistance is prevented from deteriorating. In a case where the peak metal temperature is not lower than 50 °C, the surface treatment film contains little residual moisture and thus corrosion resistance is prevented from deteriorating. The temperature (the peak metal temperature) during the heating process for drying is preferably set in the range of 60 to 180 °C.

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[0042] Therefore, it is possible to obtain by the aforementioned treatments a zinc or zinc alloy plated steel sheet having a Zr-containing film and being excellent in oil-retaining properties in a high-temperature environment or a high-temperature and high-humidity environment.

5 **[0043]** Next, a zinc or zinc alloy plated steel sheet of the present invention will be described. Such a steel sheet can be obtained according to the aforementioned method of producing a zinc or zinc alloy plated steel sheet, using the aforementioned surface treatment liquid.

The zinc or zinc alloy plated steel sheet thus obtained has a coating film formed on
10 a surface thereof, the coating film comprising in conditions satisfying (11) to (15) below:
(a) a zirconium compound; (b) silica fine particles; (c) a component derived from a silane coupling agent; (d) a vanadic acid compound; (e) a phosphoric acid compound; (f) a nickel compound; (g) an acrylic resin; and (h) a component derived from an organopolysiloxane compound. The film coating quantity in terms of zirconium content
15 per one surface is set in the range of 10 to 200 mg/m². Further, the zinc or zinc alloy plated steel sheet of the present invention may contain solid content (i_s) of the wax (i) in a condition satisfying (16) below.

[0044] (11) a mass ratio (d_v/a_{Zr}) of mass (d_v) in terms of vanadium standard of the vanadic acid compound (d) with respect to mass (a_{Zr}) in terms of zirconium standard
20 of the zirconium compound (a) is in the range of 0.04 to 0.15;

(12) a mass ratio (e_p/a_{Zr}) of mass (e_p) in terms of phosphorus standard of the phosphoric acid compound (e) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.11 to 0.55;

(13) a mass ratio (f_{Ni}/a_{Zr}) of mass (f_{Ni}) in terms of nickel standard of the nickel
25 compound (f) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.015 to 0.065;

(14) a proportion in weight of the acrylic resin (g) in the total solid contents of the film is in the range of 0.5 to 10 mass %;

(15) a mass ratio (Si_t/a_{Zr}) of the total mass (Si_t) in terms of silicon standard of the
30 silica fine particles (b), the component derived from the silane coupling agent (c) and the component derived from the organopolysiloxane compound (h) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.23 to 1.0; and

(16) a proportion of solid content (i_s) of a wax (i) in the total solid contents of the film is in the range of 2.5 to 10 mass %.

[0045] The aforementioned components (a) to (i) are subjected to the same restrictions regarding contents and mass ratios thereof as the aforementioned components (A) to (I) of the surface treatment liquid for the same reasons as in the

[0046] The reason why the zinc or zinc alloy plated steel sheet according to the present invention exhibits excellent oil-retaining properties in a high-temperature environment or a high-temperature and high-humidity environment has not been fully revealed but the inventors assume that oil-retaining properties of the zinc alloy plated steel sheet of the present invention improve probably because the surface treatment film exhibits significantly enhanced affinity with lubricating oil.

It is assumed that an organopolysiloxane compound blended in the surface treatment liquid particularly improves oil-retaining properties of the steel sheet because alkyl group of the organopolysiloxane compound exhibits significantly enhanced affinity with lubricating oil. Further, it is assumed that the effect of improving oil-retaining properties of the steel sheet caused by an organopolysiloxane compound in a high-temperature environment or a high-temperature and high-humidity environment results from formation of siloxane bond by a reaction between the organopolysiloxane compound and the silane coupling agent.

[0047] It is assumed that the water-soluble zirconium compound is bonded to the water-dispersible silica fine particles and the silane coupling agent, thereby functioning as a binder of the surface treatment film. Such an inorganic film as formed in the aforementioned manner exhibits less adhesion to and accumulation in a treated product or a mold than a film containing relatively large amount of organic substances.

Further, in a case where the surface treatment film contains wax, stress exerted on the film is alleviated, whereby appearance after press molding and corrosion resistance of the steel sheet can improve.

[0048] Regarding the coating quantity of the surface treatment film on the zinc or zinc alloy plated steel sheet, it is critically important that the content of the zirconium compound in the surface treatment film in terms of zirconium standard, i.e. the film coating quantity (Zr), is within the range of 10 to 200 mg/m² for the same reasons as the reasons for specifying the film coating quantity of the surface treatment film described in

connection with the surface treatment liquid.

Example 1

[0049] An effect of the present invention will be described by Examples and Comparative Examples hereinafter. These Examples are provided only for an
5 explanatory purpose with no particular limitation thereto.

[0050] 1. Method of preparing a test sheet

(1) Sample material (Base material)

Following commercially available materials are used as sample materials.

- (i) Electrolytic galvanized steel sheet (EG) having sheet thickness: 0.8 mm and
10 coating weight of zinc: 20/20 (g/m^2)
- (ii) Hot-dip galvanized steel sheet (GI) having sheet thickness: 0.8 mm, and coating weight of zinc: 60/60 (g/m^2)

In the present invention, “an electrolytic galvanized steel sheet has a coating weight of zinc: 20/20 (g/m^2)” means that the steel sheet has 20 (g/m^2) of plating provided on top
15 and rear surfaces thereof, respectively.

[0051] (2) Pretreatment (washing)

In a method of preparing a test piece, surfaces of the aforementioned sample material are treated by using “PALKLINN364S” manufactured by Nihon Parkerizing Co., Ltd. so that oil, dust and dirt on the surfaces are removed. After confirming that the surfaces of
20 the metal material 100% get wet by water by washing them with tap water, the surfaces are further wetted with pure water and the moisture is then removed by drying the metal material in an oven heated at 100 °C.

[0052] (3) Surface treatment liquid of the present invention

Various surface treatment liquids for a zinc or zinc alloy plated steel sheet, having the
25 compositions (mass ratios) as shown in Table 1-1, Table 1-2 and Table 1-3, are prepared. Solid content in each of the surface treatment liquids is 5 mass %.

[0053]

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Level of measurement		Surface treatment liquid for galvanized steel sheet																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
		Component (A)		Component (B)		Component (C)		Component (D)		Component (E)		Component (F)		Component (G)		Component (H)		Component (I)		B _s /A _{Zr}		C/A _{Zr}		D _v /A _{Zr}		E _p /A _{Zr}		F _{Ni} /A _{Zr}		Si _{Ir} /A _{Zr}		G _s		H _s		I _s		pH																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																
		Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio		Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio

Surface treatment liquid for galvanized steel sheet

Level of measurement		Surface treatment liquid for galvanized steel sheet																																					
		Component (A)		Component (B)		Component (C)		Component (D)		Component (E)		Component (F)		Component (G)		Component (H)		Component (I)		B _s /A _{Zr}		C/A _{Zr}		D _v /A _{Zr}		E _p /A _{Zr}		F _{Ni} /A _{Zr}		Si _{Tr} /A _{Zr}		C _s		H _s		I _s		pH	
Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %	Mass ratio	Mass %		
Example 29	A1	B1	C1	D1	E1	F2	G1	H1	I1	0.6	1.2	0.10	0.21	0.032	0.47	4.1	1.0	4.9	8.4																				
Example 30	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.37	0.032	0.47	3.9	0.9	4.7	8.4																				
Example 31	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.55	0.032	0.47	3.8	0.9	4.5	8.4																				
Example 32	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 33	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 34	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.016	0.47	4.1	1.0	4.9	8.4																				
Example 35	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.023	0.47	4.1	1.0	4.9	8.4																				
Example 36	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.023	0.47	4.1	1.0	4.9	8.4																				
Example 37	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.049	0.47	4.0	1.0	4.8	8.4																				
Example 38	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.065	0.47	3.9	0.9	4.7	8.4																				
Example 39	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	0.5	4.8	8.4																				
Example 40	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	0.7	4.8	8.4																				
Example 41	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	3.8	4.6	4.6	8.4																				
Example 42	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	3.8	6.4	4.6	8.4																				
Example 43	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 44	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 45	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 46	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 47	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	0.5	1.0	4.8	8.4																				
Example 48	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4																				
Example 49	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	9.5	1.0	4.8	8.4																				
Example 50	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	2.1	1.0	2.5	8.4																				
Example 51	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	2.8	1.0	3.4	8.4																				
Example 52	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	5.9	0.9	7.1	8.4																				
Example 53	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	7.7	0.9	9.2	8.4																				
Example 54	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	7.9	0.9	9.5	8.4																				
Comp. Ex 55	A1	B1	C1	D1	E1	F1	G1	H1	I1	3.0	6.2	0.25	1.34	0.162	2.33	5.9	1.4	7.1	8.4																				
Comp. Ex 56	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.2	0.4	0.03	0.09	0.011	0.16	2.3	0.5	2.7	8.4																				

[0055]

[Table 1-3]

Table 1-3

Level of measurement		Surface treatment liquid for galvanized steel sheet																			
		Component (A)		Component (B)		Component (C)		Component (D)		Component (E)		Component (F)		Component (G)		Component (H)		Component (I)		B _s /A _{Zr}	
		Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Type	Mass ratio	Mass %
		C/A _{Zr}		D _V /A _{Zr}		E _P /A _{Zr}		F _{NI} /A _{Zr}		S _{IT} /A _{Zr}		G _s		H _s		I _s		pH			
		Mass ratio		Mass ratio		Mass ratio		Mass ratio		Mass ratio		Mass %		Mass %		Mass %		Mass %			
Comp. Ex 57	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.02	0.27	0.032	0.47	4.1	1.0	4.9	8.4		
Comp. Ex 58	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.30	0.27	0.032	0.47	3.8	9.0	4.6	8.4		
Comp. Ex 59	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	0.3	0.10	0.27	0.032	0.32	5.1	1.2	6.1	8.4		
Comp. Ex 60	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	3.7	0.10	0.27	0.032	0.83	2.7	0.6	3.2	8.4		
Comp. Ex 61	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.09	0.032	0.47	4.3	1.0	5.1	8.4		
Example 62	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	4.0		
Example 63	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	12		
Comp. Ex 64	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.75	0.032	0.47	3.6	0.9	4.3	8.4		
Comp. Ex 65	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.006	0.47	4.1	1.0	4.9	8.4		
Example 66	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 67	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Comp. Ex 68	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Comp. Ex 69	A2	B1	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Comp. Ex 70	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.097	0.47	3.8	0.9	4.6	8.4		
Comp. Ex 71	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.1	0.2	4.9	8.4		
Comp. Ex 72	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	3.8	7.2	4.5	8.4		
Comp. Ex 73	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	0.8	1.0	1.0	8.4		
Comp. Ex 74	A1	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	15.0	8.4		
Example 75	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 76	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 77	A2	B1	C1	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 78	A2	B1	C1	D1	E1	F1	G2	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 79	A2	B1	C1	D1	E1	F1	G3	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 80	A2	B1	C1	D1	E1	F1	G4	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Comp. Ex 81	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	0.4	1.0	4.8	8.4		
Comp. Ex 82	A2	B2	C2	D1	E1	F1	G1	H1	I1	0.6	1.2	0.10	0.27	0.032	0.47	15.0	1.0	4.8	8.4		
Example 83	A2	B2	C2	D1	E1	F1	G1	H2	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		
Example 84	A2	B2	C2	D1	E1	F1	G1	H3	I1	0.6	1.2	0.10	0.27	0.032	0.47	4.0	1.0	4.8	8.4		

[0056] The compounds shown in Table 1-1, Table 1-2, and Table 1-3 are as follows.

<Water-soluble zirconium compound (A)>

A1: sodium zirconium carbonate

A2: ammonium zirconium carbonate

5 **[0057]** <Water-dispersible silica fine particles (B)>

B1: SNOWTEX N®

B2: SNOWTEX O®

[0058] <Silane coupling agent (C)>

C1: γ -aminopropyltriethoxysilane

10 C2: γ -glycidoxypolytrimethoxysilane

[0059] <Vanadic acid compound (D)>

D1: sodium metavanadate

D2: ammonium metavanadate

[0060] <Phosphoric acid compound (E)>

15 E1: 1-hydroxymethane-1,1-diphosphonic acid

E2: Phosphoric acid

[0061] <Nickel compound (F)>

F1: nickel nitrate hexahydrate

F2: nickel sulfate hexahydrate

20 **[0062]** <Acrylic resin emulsion (G)>

G1: styrene-ethylmethacrylate-n-butylacrylate-acrylic acid

(T_g: 18°C)

G2: methylmethacrylate-2-ethylhexylacrylate-acrylic acid

(T_g: 14°C)

25 G3: styrene-ethylmethacrylate-n-butylacrylate-acrylic acid

(T_g: 5°C)

G4: styrene-ethylmethacrylate-n-butylacrylate-acrylic acid

(T_g: 40°C)

[0063] <Organopolysiloxane compound (H)>

30 H1: methylphenyl silicone oil (viscosity: 100 mm²/s)

H2: dimethyl silicone oil (viscosity: 0.65 mm²/s)

H3: methylphenyl silicone oil (viscosity: 500,000 mm²/s)

[0064] <Wax (I)>

I1: polyethylene wax (CHEMIPEARL W900®)

[0065] (4) Treatment method

Each of the test sheets is coated with the surface treatment liquid described above by
boar coating, put into an oven without being washed with water, and dried at the drying
5 temperature shown in Table 2-1 and Table 2-2, so that a surface treatment film having a
“film coating quantity (Zr)” (Zr content) shown in Table 3-1 and Table 3-2 is formed
thereon.

The “film coating quantity (Zr)” of the surface treatment film of each test sheet is
adjusted by the concentration of the surface treatment liquid and an actual “film coating
10 quantity (Zr)”, i.e. actual content of the zirconium compound in the surface treatment
film in terms of zirconium standard, of the surface treatment film is quantitatively
analyzed by an X-ray fluorescence analyzer with reference to the standard curve
obtained from a standard steel sheet of which “film coating quantity (Zr)” is known.
The drying condition is adjusted by the temperature of the oven and a duration time
15 during which each test sheet stays in the oven. The drying temperature represents the
end-point temperature at a surface of each test sheet. The bar coating process is actually
carried out as follows.

[0066] The surface treatment liquid (agent) is applied dropwise to each test sheet
and coated on the test sheet by a #3-#5 bar coater. The coating process is adjusted by the
20 number of the bar coater in use and the concentration of the surface treatment liquid such
that a resulting surface treatment film has a predetermined “film coating quantity (Zr)”.
Types of the test sheets (sample materials), coating methods, and the drying
temperatures during formation of surface treatment films are shown for the respective
levels of measurement in Table 2-1 and Table 2-2. Compositions and Zr contents of the
25 surface treatment films of the galvanized steel sheets thus obtained are shown in Table 3-
1 and Table 3-2.

[0067]

[Table 2-1]

Table 2-1

Level of measurement		Sample material	Treatment method	
			Coating method	Drying temperature
		Type	Type	°C
Example	1	(i)	Bar coating	140
Example	2	(i)	Bar coating	140
Example	3	(i)	Bar coating	140
Example	4	(i)	Bar coating	140
Example	5	(i)	Bar coating	140
Example	6	(i)	Bar coating	140
Example	7	(i)	Bar coating	140
Example	8	(i)	Bar coating	140
Example	9	(i)	Bar coating	140
Example	10	(i)	Bar coating	140
Example	11	(i)	Bar coating	140
Example	12	(i)	Bar coating	140
Example	13	(i)	Bar coating	140
Example	14	(i)	Bar coating	140
Example	15	(i)	Bar coating	140
Example	16	(i)	Bar coating	140
Example	17	(i)	Bar coating	140
Example	18	(i)	Bar coating	140
Example	19	(i)	Bar coating	140
Example	20	(i)	Bar coating	140
Example	21	(i)	Bar coating	140
Example	22	(i)	Bar coating	140
Example	23	(i)	Bar coating	140
Example	24	(i)	Bar coating	140
Example	25	(i)	Bar coating	140
Example	26	(i)	Bar coating	140
Example	27	(i)	Bar coating	140
Example	28	(i)	Bar coating	140
Example	29	(i)	Bar coating	140
Example	30	(i)	Bar coating	140
Example	31	(i)	Bar coating	140
Example	32	(i)	Bar coating	140
Example	33	(i)	Bar coating	140
Example	34	(i)	Bar coating	140
Example	35	(i)	Bar coating	140
Example	36	(i)	Bar coating	140
Example	37	(i)	Bar coating	140
Example	38	(i)	Bar coating	140
Example	39	(i)	Bar coating	140
Example	40	(i)	Bar coating	140
Example	41	(i)	Bar coating	140
Example	42	(i)	Bar coating	140

[0068] [Table 2-2]

Table 2-2

Level of measurement		Sample material	Treatment method	
			Coating method	Drying temperature
		Type	Type	°C
Example	43	(i)	Bar coating	50
Example	44	(i)	Bar coating	60
Example	45	(i)	Bar coating	180
Example	46	(i)	Bar coating	250
Example	47	(i)	Bar coating	180
Example	48	(i)	Bar coating	180
Example	49	(i)	Bar coating	180
Example	50	(i)	Bar coating	140
Example	51	(i)	Bar coating	140
Example	52	(i)	Bar coating	140
Example	53	(i)	Bar coating	140
Example	54	(i)	Bar coating	140
Comp. Ex.	55	(i)	Bar coating	140
Comp. Ex.	56	(i)	Bar coating	140
Comp. Ex.	57	(i)	Bar coating	140
Comp. Ex.	58	(i)	Bar coating	140
Comp. Ex.	59	(i)	Bar coating	140
Comp. Ex.	60	(i)	Bar coating	140
Comp. Ex.	61	(i)	Bar coating	140
Example	62	(i)	Bar coating	140
Example	63	(i)	Bar coating	140
Comp. Ex.	64	(i)	Bar coating	140
Comp. Ex.	65	(i)	Bar coating	140
Example	66	(i)	Bar coating	140
Example	67	(i)	Bar coating	140
Comp. Ex.	68	(i)	Bar coating	140
Comp. Ex.	69	(i)	Bar coating	140
Comp. Ex.	70	(i)	Bar coating	140
Comp. Ex.	71	(i)	Bar coating	140
Comp. Ex.	72	(i)	Bar coating	140
Comp. Ex.	73	(i)	Bar coating	140
Comp. Ex.	74	(i)	Bar coating	140
Example	75	(i)	Bar coating	40
Example	76	(i)	Bar coating	300
Example	77	(i)	Bar coating	140
Example	78	(i)	Bar coating	140
Example	79	(i)	Bar coating	140
Example	80	(i)	Bar coating	140
Comp. Ex.	81	(i)	Bar coating	180
Comp. Ex.	82	(i)	Bar coating	180
Example	83	(i)	Bar coating	140
Example	84	(i)	Bar coating	140

[0069] [Table 3-1]

Table 3-1

Level of measurement		Surface film of galvanized steel sheet						
		b/a_z	d/a_z	e/a_z	f/a_z	S/a_z	i	Film coating quantity (Zr)
		Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass %	mg/m^2
Example	1	1.2	0.15	0.54	0.065	0.93	6.0	80
Example	2	0.9	0.14	0.38	0.046	0.67	5.5	80
Example	3	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	4	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	5	0.4	0.07	0.18	0.022	0.31	4.0	80
Example	6	0.4	0.07	0.18	0.022	0.31	4.0	80
Example	7	0.3	0.05	0.13	0.016	0.23	3.4	80
Example	8	0.3	0.10	0.27	0.032	0.32	5.2	80
Example	9	0.4	0.10	0.27	0.032	0.38	5.0	80
Example	10	0.4	0.10	0.27	0.032	0.38	5.0	80
Example	11	0.9	0.10	0.27	0.032	0.61	4.5	80
Example	12	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	13	0.6	0.05	0.27	0.032	0.47	4.9	80
Example	14	0.6	0.07	0.27	0.032	0.47	4.9	80
Example	15	0.6	0.07	0.27	0.032	0.47	4.9	80
Example	16	0.6	0.15	0.27	0.032	0.47	4.8	80
Example	17	0.6	0.20	0.27	0.032	0.47	4.7	80
Example	18	0.6	0.10	0.27	0.032	0.38	5.6	80
Example	19	0.6	0.10	0.27	0.032	0.41	5.2	80
Example	20	0.6	0.10	0.27	0.032	0.41	5.2	80
Example	21	0.6	0.10	0.27	0.032	0.41	5.2	80
Example	22	0.6	0.10	0.27	0.032	0.56	4.3	80
Example	23	0.6	0.10	0.27	0.032	0.65	3.8	80
Example	24	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	25	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	26	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	27	0.6	0.10	0.12	0.032	0.47	5.0	80
Example	28	0.6	0.10	0.21	0.032	0.47	4.9	80
Example	29	0.6	0.10	0.21	0.032	0.47	4.9	80
Example	30	0.6	0.10	0.37	0.032	0.47	4.7	80
Example	31	0.6	0.10	0.55	0.032	0.47	4.5	80
Example	32	0.6	0.10	0.27	0.032	0.47	4.8	30
Example	33	0.6	0.10	0.27	0.032	0.47	4.8	150
Example	34	0.6	0.10	0.27	0.016	0.47	4.9	80
Example	35	0.6	0.10	0.27	0.023	0.47	4.9	80
Example	36	0.6	0.10	0.27	0.023	0.47	4.9	80
Example	37	0.6	0.10	0.27	0.049	0.47	4.8	80
Example	38	0.6	0.10	0.27	0.065	0.47	4.7	80
Example	39	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	40	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	41	0.6	0.10	0.27	0.032	0.47	4.6	80
Example	42	0.6	0.10	0.27	0.032	0.47	4.6	80

[0070] [Table 3-2]

Table 3-2

Level of measurement		Surface film of galvanized steel sheet						Film coating quantity (Zr)
		b/a_{Zr}	d/a_{Zr}	e/a_{Zr}	f/a_{Zr}	S/a_{Zr}	j	
		Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass ratio	Mass %	mg/m ²
Example	43	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	44	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	45	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	46	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	47	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	48	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	49	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	50	0.6	0.10	0.27	0.032	0.47	2.5	80
Example	51	0.6	0.10	0.27	0.032	0.47	3.4	80
Example	52	0.6	0.10	0.27	0.032	0.47	7.1	80
Example	53	0.6	0.10	0.27	0.032	0.47	9.2	80
Example	54	0.6	0.10	0.27	0.032	0.47	9.5	80
Com p. Ex	55	3.0	0.25	1.34	0.162	2.33	7.1	80
Com p. Ex	56	0.2	0.03	0.09	0.011	0.16	2.7	80
Com p. Ex	57	0.6	0.02	0.27	0.032	0.47	4.9	80
Com p. Ex	58	0.6	0.30	0.27	0.032	0.47	4.6	80
Com p. Ex	59	0.6	0.10	0.27	0.032	0.32	6.1	80
Com p. Ex	60	0.6	0.10	0.27	0.032	0.83	3.2	80
Com p. Ex	61	0.6	0.10	0.09	0.032	0.47	5.1	80
Example	62	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	63	0.6	0.10	0.27	0.032	0.47	4.8	80
Com p. Ex	64	0.6	0.10	0.75	0.032	0.47	4.3	80
Com p. Ex	65	0.6	0.10	0.27	0.006	0.47	4.9	80
Example	66	0.6	0.10	0.27	0.032	0.47	4.8	10
Example	67	0.6	0.10	0.27	0.032	0.47	4.8	200
Com p. Ex	68	0.6	0.10	0.27	0.032	0.47	4.8	5
Com p. Ex	69	0.6	0.10	0.27	0.032	0.47	4.8	250
Com p. Ex	70	0.6	0.10	0.27	0.097	0.47	4.6	80
Com p. Ex	71	0.6	0.10	0.27	0.032	0.47	4.9	80
Com p. Ex	72	0.6	0.10	0.27	0.032	0.47	4.5	80
Com p. Ex	73	0.6	0.10	0.27	0.032	0.47	1.0	80
Com p. Ex	74	0.6	0.10	0.27	0.032	0.47	4.0	80
Example	75	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	76	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	77	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	78	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	79	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	80	0.6	0.10	0.27	0.032	0.47	4.8	80
Com p. Ex	81	0.6	0.10	0.27	0.032	0.47	4.8	80
Com p. Ex	82	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	83	0.6	0.10	0.27	0.032	0.47	4.8	80
Example	84	0.6	0.10	0.27	0.032	0.47	4.8	80

[0071] (5) Method of carrying out evaluating tests

(5-1) Evaluation of corrosion resistance

A sample piece (70 × 150 mm) was cut out of each test sheet produced according to the
aforementioned method. The sample piece, of which the rear surface and end portions
5 had been sealed by vinyl tapes, was subjected to following tests. The proportion of an
area where rust appeared, with respect to the entire top surface, was visually measured
for evaluation.

Salt spray test (according to SST: JIS-Z-2371)

The proportion of an area where whiter rust appeared 72 hours after SST, with respect to
10 the entire top surface of the sample piece, was visually determined and evaluated
according to the judgment criteria below.

The judgment criteria are as follows.

- ◎: Proportion of area where rust appeared is less than 5 %
- 15 ○: Proportion of area where rust appeared is within the range of 5 to 20 % (inclusive
of 5% and exclusive of 20%)
- : Proportion of area where rust appeared is within the range of 20 to 30 % (inclusive
of 20% and exclusive of 30%)
- △: Proportion of area where rust appeared is within the range of 30 to 40 % (inclusive
20 of 30% and exclusive of 40%)
- × : Proportion of area where rust appeared is 40 % or more

[0072] (5-2) Oil-retaining properties in a high-temperature environment

A lubricating oil (“ALL TIME J 652” manufactured by NOK Corporation) having
kinematic viscosity at 40°C: 51-69 mm²/s and kinematic viscosity at 100°C: 11.1-14.9
25 mm²/s, respectively, was put in a vessel. Each test sheet prepared as described above was
also put in the vessel and left therein for 3 days at 85°C in a state where the test sheet
stood upright with the lower end portion thereof immersed in the lubricating oil. A
height which the lubricating oil reached by oozing marked in the test sheet was measured.
The judgment criteria are as follows.

30

- ◎: Oozing height is less shorter than 0.5 cm
- : Oozing height is within the range of 0.5 to 1.0 cm (inclusive of 0.5 cm and
exclusive of 1.0 cm)

○—: Oozing height is within the range of 1.0 to 1.5 cm (inclusive of 1.0 cm and exclusive of 1.5 cm)

△: Oozing height is within the range of 1.5 to 3.0 cm (inclusive of 1.5 cm and exclusive of 3.0 cm)

5 ✕ : Oozing height is 3.0 cm or more

[0073] (5-3) Oil-retaining properties in a high-temperature and high-humidity environment

A lubricating oil (“ALL TIME J 652” manufactured by NOK Corporation) having kinematic viscosity at 40°C: 51-69 mm²/s and kinematic viscosity at 100°C: 11.1-14.9 mm²/s, respectively, was put in a vessel. Each test sheet prepared as described above was also put in the vessel and left therein for 3 days at 60°C and relative humidity 90% in a state where the test sheet stood upright with the lower end portion thereof immersed in the lubricating oil. A height which the lubricating oil reached by oozing marked in the test sheet was measured. The judgment criteria are as follows.

15

◎: Oozing height is less shorter than 0.5 cm

○: Oozing height is within the range of 0.5 to 1.0 cm (inclusive of 0.5 cm and exclusive of 1.0 cm)

20 ○—: Oozing height is within the range of 1.0 to 1.5 cm (inclusive of 1.0 cm and exclusive of 1.5 cm)

△: Oozing height is within the range of 1.5 to 3.0 cm (inclusive of 1.5 cm and exclusive of 3.0 cm)

✕ : Oozing height is 3.0 cm or more

[0074] (5-4) Appearance after press molding (continuous high-speed press)

25 Multi-stage drawing of each test sheet was carried out in the press conditions shown below in a state where the test sheet was coated with lubricating oil. This drawing operation was repeated ten times continuously without wiping out dirt attaching to a mold. Degree of peeling dirt adhered to a surface of the molded member after the 10th drawing and degree of blackening of the surface of the molded member were visually observed and evaluated.

30

[Press condition]

Thickness of the zinc or zinc alloy plated steel sheet: 0.8 mm

Molding rate: 450 mm/second

Blank diameter ϕ : 90 mm

(1st drawing) Punch diameter ϕ : 49 mm, Clearance between punch and dice: 1.0 mm

(2nd drawing) Punch diameter ϕ : 39 mm, Clearance between punch and dice: 0.8 mm

(3rd drawing) Punch diameter ϕ : 32 mm, Clearance between punch and dice: 0.8 mm

5 (4th drawing) Punch diameter ϕ : 27.5 mm, Clearance between punch and dice: 0.8 mm

(5th drawing) Punch diameter ϕ : 24.4 mm, Clearance between punch and dice: 0.8 mm

[0075] Evaluation criteria are as follows.

- 10 ◎: Hardly any peeling dirt accumulated in lubricating oil is adhered to surface of molded member and blackening of the surface of the molded member is not observed, either.
- : Very small amount of peeling dirt accumulated in lubricating oil is adhered to surface of molded member, while blackening of the surface of the molded member is not observed.
- 15 ○—: Small amount of peeling dirt accumulated in lubricating oil is adhered to surface of molded member and light blackening of the surface of the molded member is observed.
- △: Some amount of peeling dirt accumulated in lubricating oil is adhered to surface of molded member and moderate blackening of the surface of the molded member is observed.
- 20 ✕ : Large amount of peeling dirt accumulated in lubricating oil is adhered to surface of molded member and significant blackening of the surface of the molded member is observed.

[0076] The quality (corrosion resistance, oil-retaining properties and appearance after press molding) of the surface-treated zinc or zinc alloy plated steel sheet thus
25 obtained were investigated. The results are shown in Table 4-1 and Table 4-2.

[0077]

[Table 4-1]

Table 4-1

Level of measurement		Corrosion resistance	Appearance after press molding	Oil-retaining properties (85°C)	Oil-retaining properties (60°C × 90%RH)
Example	1	○	○	◎	◎
Example	2	◎	○	◎	◎
Example	3	◎	◎	◎	◎
Example	4	◎	◎	◎	◎
Example	5	○	◎	◎	◎
Example	6	○	◎	◎	◎
Example	7	○	○	◎	◎
Example	8	○	○	○	○
Example	9	◎	◎	◎	◎
Example	10	◎	◎	◎	◎
Example	11	◎	◎	◎	◎
Example	12	◎	◎	◎	◎
Example	13	○	◎	◎	◎
Example	14	◎	◎	◎	◎
Example	15	◎	◎	◎	◎
Example	16	◎	○	◎	◎
Example	17	○	◎	◎	◎
Example	18	◎	○	○	○
Example	19	◎	◎	◎	◎
Example	20	◎	◎	◎	◎
Example	21	◎	◎	◎	◎
Example	22	○	◎	◎	◎
Example	23	○—	◎	◎	◎
Example	24	○	◎	◎	◎
Example	25	◎	◎	◎	◎
Example	26	◎	◎	◎	◎
Example	27	○	◎	◎	◎
Example	28	◎	◎	◎	◎
Example	29	◎	◎	◎	◎
Example	30	◎	◎	◎	◎
Example	31	◎	○	◎	◎
Example	32	◎	◎	◎	◎
Example	33	◎	◎	◎	◎
Example	34	○	◎	◎	◎
Example	35	◎	◎	◎	◎
Example	36	◎	◎	◎	◎
Example	37	◎	◎	◎	◎
Example	38	○	◎	◎	◎
Example	39	◎	○	◎	◎
Example	40	◎	◎	◎	◎
Example	41	◎	◎	◎	◎
Example	42	○	◎	◎	◎

[0078] [Table 4-2]

Table 4-2

Level of measurement	Corrosion resistance	Appearance after press molding	Oil-retaining properties (85°C)	Oil-retaining properties (60°C×90%RH)
Example	43	○	◎	◎
Example	44	◎	◎	◎
Example	45	◎	◎	◎
Example	46	○	◎	◎
Example	47	○	◎	◎
Example	48	◎	◎	◎
Example	49	◎	○	◎
Example	50	◎	○	◎
Example	51	◎	◎	◎
Example	52	◎	◎	◎
Example	53	○	◎	◎
Example	54	○	◎	◎
Comp. Ex.	55	×	△	◎
Comp. Ex.	56	×	×	×
Comp. Ex.	57	×	◎	◎
Comp. Ex.	58	△	×	◎
Comp. Ex.	59	○	△	×
Comp. Ex.	60	×	○	○—
Comp. Ex.	61	×	○—	◎
Example	62	○	○	◎
Example	63	○	◎	◎
Comp. Ex.	64	◎	×	◎
Comp. Ex.	65	×	◎	◎
Example	66	○—	◎	○—
Example	67	◎	○—	◎
Comp. Ex.	68	×	◎	×
Comp. Ex.	69	◎	×	◎
Comp. Ex.	70	△	◎	◎
Comp. Ex.	71	◎	○—	△
Comp. Ex.	72	△	○—	◎
Comp. Ex.	73	○—	△	◎
Comp. Ex.	74	△	○	◎
Example	75	△	○	◎
Example	76	△	◎	◎
Example	77	◎	◎	◎
Example	78	◎	◎	◎
Example	79	◎	◎	◎
Example	80	◎	◎	◎
Comp. Ex.	81	△	◎	◎
Comp. Ex.	82	◎	×	◎
Example	83	◎	◎	◎
Example	84	○	◎	◎

[0079] As shown in Table 4-1 and Table 4-2, the zinc or zinc alloy plated steel sheets of Examples, each having a Zr-containing film formed by using the surface treatment liquid including specific components according to the present invention, respectively exhibit not only good corrosion resistance and good appearance after press molding but also excellent oil-retaining properties in a high-temperature environment and a high-temperature and high-humidity environment.

In contrast, each of the zinc or zinc alloy plated steel sheets of Comparative Examples exhibits poor results at least one of corrosion resistance, appearance after press molding and oil-retaining properties.

10 Industrial Applicability

[0080] According to the present invention, a zinc or zinc alloy plated steel sheet having good oil-retaining properties in a high-temperature environment or a high-temperature and high-humidity environment can be provided. As a result, smooth sliding movement of a rotating shaft with respect to a bearing can be ensured for a relatively long period, whereby vibrations and noises of various motors for use in automobiles, AV (audio-visual) and OA (office automation) devices, and the like can be reduced and the product life of these motors can be prolonged.

Claims

1. A surface treatment liquid for a zinc or zinc alloy plated steel sheet, comprising in conditions satisfying (1) to (8) below:
 - 5 (A) a water-soluble zirconium compound;
 - (B) a water-dispersible silica fine particles;
 - (C) a silane coupling agent;
 - (D) a vanadic acid compound;
 - (E) a phosphoric acid compound;
 - 10 (F) a nickel compound;
 - (G) an acrylic resin emulsion; and
 - (H) an organopolysiloxane compound,wherein: (1) a mass ratio $(B_S)/(A_{Zr})$ of mass of a solid content (B_S) of the water-dispersible silica fine particles (B) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.3 to 1.2;
- 15 (2) a mass ratio $(C)/(A_{Zr})$ of mass of a silane coupling agent (C) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.6 to 2.5;
- (3) a mass ratio $(D_V)/(A_{Zr})$ of mass (D_V) in terms of vanadium standard of the vanadic acid compound (D) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.04 to 0.15;
- 20 (4) a mass ratio $(E_P)/(A_{Zr})$ of mass (E_P) in terms of phosphorus standard of the phosphoric acid compound (E) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.11 to 0.55;
- 25 (5) a mass ratio $(F_{Ni})/(A_{Zr})$ of mass (F_{Ni}) in terms of nickel standard of the nickel compound (F) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.015 to 0.065;
- (6) a proportion of solid content (G_S) of the acrylic resin emulsion (G) in the total solid contents of the surface treatment liquid is in the range of 0.5 to 10 mass %;
- 30 (7) a proportion of solid content (H_S) of the organopolysiloxane compound (H) in the total solid contents of the surface treatment liquid is in the range of 0.55 to 6.5 mass %; and
- (8) a mass ratio $(Si_T)/(A_{Zr})$ of the total mass (Si_T) in terms of silicon standard of

the water-dispersible silica fine particles (B), the silane coupling agent (C) and the organopolysiloxane compound (H) with respect to mass (A_{Zr}) in terms of zirconium standard of the water-soluble zirconium compound (A) is in the range of 0.23 to 1.0.

- 5 2. The surface treatment liquid for a zinc or zinc alloy plated steel sheet of claim 1, further comprising a wax (I) in a condition satisfying (9) below,
 wherein (9) a proportion of solid content (I_s) of the wax in the total solid contents of the surface treatment liquid is in the range of 2.5 to 10 mass %.

- 10 3. A method of producing a surface-treated zinc or zinc alloy plated steel sheet, comprising:
 coating a surface of a zinc or zinc alloy plated steel sheet with the surface treatment liquid of claim 1 or 2; and
 drying the zinc or zinc alloy plated steel sheet thus coated by heating,
15 wherein a film coating quantity in terms of zirconium content per one surface is in the range of 10 to 200 mg/m².

4. A zinc or zinc alloy plated steel sheet having a film formed on a surface thereof, the film comprising in conditions satisfying (11) to (15) below:

- 20 (a) a zirconium compound;
 (b) silica fine particles;
 (c) a component derived from a silane coupling agent;
 (d) a vanadic acid compound;
 (e) a phosphoric acid compound;
25 (f) a nickel compound;
 (g) an acrylic resin; and
 (h) a component derived from an organopolysiloxane compound,
 wherein: (11) a mass ratio (d_v)/(a_{Zr}) of mass (d_v) in terms of vanadium standard of the vanadic acid compound (d) with respect to mass (a_{Zr}) in terms of zirconium standard
30 of the zirconium compound (a) is in the range of 0.04 to 0.15;
 (12) a mass ratio (e_p)/(a_{Zr}) of mass (e_p) in terms of phosphorus standard of the phosphoric acid compound (e) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.11 to 0.55;

(13) a mass ratio (f_{Ni})/(a_{Zr}) of mass (f_{Ni}) in terms of nickel standard of the nickel compound (f) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of 0.015 to 0.065;

5 (14) a proportion in weight of the acrylic resin (g) in the total solid contents of the film is in the range of 0.5 to 10 mass %;

(15) a mass ratio (Si_t)/(a_{Zr}) of the total mass (Si_t) in terms of silicon standard of the silica fine particles (b), the component derived from the silane coupling agent (c) and the component derived from the organopolysiloxane compound (h) with respect to mass (a_{Zr}) in terms of zirconium standard of the zirconium compound (a) is in the range of
10 0.23 to 1.0; and

a film coating quantity in terms of zirconium content per one surface is in the range of 10 to 200 mg/m².

5. The zinc or zinc alloy plated steel sheet of claim 4, wherein the film further
15 comprises a wax (i) in a condition satisfying (16) below,

wherein (16) a proportion of solid content (i_s) of the wax (i) in the total solid contents of the film is in the range of 2.5 to 10 mass %.