

Specification

[Title of the Invention] AQUEOUS COATING AGENT FOR STEEL MATERIAL,
COATING FILM, STEEL MATERIAL COATING METHOD, AND STEEL
MATERIAL

[Technical Field of the Invention]

[0001]

The present invention relates to an aqueous coating agent for a steel material,
a coating film, a steel material coating method, and a steel material.

Priority is claimed on Japanese Patent Application No. 2020-176150, filed
October 20, 2020, the content of which is incorporated herein by reference.

[Related Art]

[0002]

In the related art, a chromate treatment is known as a treatment for imparting
corrosion resistance to a steel material or a plated steel material. In the chromate
treatment, a surface of a steel material after the treatment is yellowish while
maintaining metallic gloss. On the other hand, since hexavalent chromium used for
the chromate treatment is toxic, a non-chromium treatment containing no chromium
has also been used in recent years (for example, refer to Patent Document 1).

[Prior Art Document]

[Patent Document]

[0003]

[Patent Document 1] Japanese Unexamined Patent Application, First
Publication No. 2004-190121

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0004]

Since a surface of a steel material subjected to the non-chromium treatment is not colored unlike in the chromate treatment but is colorless and transparent, it is difficult to visually determine the presence or absence of the treatment. In order to confirm the presence or absence of the treatment, there is a method of analyzing a surface of a steel material or using a marking device. However, this causes a problem of an increase in cost due to the addition of a process.

[0005]

Therefore, it is conceivable to color the surface of the steel material subjected to the non-chromium treatment. Here, it is preferable that the surface of the steel material can be provided with an external appearance having a vivid color tone and excellent designability while maintaining a metallic gloss peculiar to the steel material with respect to the steel material. However, in a case where a pigment is simply added to a treatment agent in order to color the steel material in the non-chromium treatment, there is a problem in that performance such as corrosion resistance and weather resistance of a formed coating film deteriorates. In addition, there is a problem in that the pigment aggregates in the coating film and causes an external appearance with unclear color and poor metallic gloss.

[0006]

The present invention has been made in view of the above, and an object thereof is to provide an aqueous coating agent for a steel material, a coating film, a method of coating a steel material, and a steel material capable of maintaining corrosion resistance and weather resistance of a coating film to be formed and imparting preferable designability to a metal surface,.

In addition, another object of the present invention is to provide a coating film

for a steel material, a method of coating a steel material, and a steel material capable of maintaining corrosion resistance and weather resistance and imparting preferable designability to a metal surface.

[Means for Solving the Problem]

[0007]

(1) The present invention relates to an aqueous coating agent for a steel material including: polyurethane resin particles (A-1) and ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) both having a median diameter of 20 to 100 nm and having a silanol group or an alkoxysilyl group or combination thereof; silicon oxide particles (B) having a mode size of 5 to 20 nm; an organic titanium compound (C); and a phthalocyanine pigment (F) coated with a resin or a surfactant or combination thereof, in which an amount of the phthalocyanine pigment (F) is 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the polyurethane resin particles (A-1) and the ethylene-unsaturated carboxylic acid copolymer resin particles (A-2), and a primary particle size of the phthalocyanine pigment (F) is 0.01 to 1.0 μm .

[0008]

According to the invention of (1), it is possible to provide an aqueous coating agent for a steel material capable of maintaining corrosion resistance and weather resistance of a coating film to be formed and imparting preferable designability to a metal surface.

[0009]

(2) The aqueous coating agent for a steel material according to [1], in which a phthalocyanine in the phthalocyanine pigment (F) is a metal phthalocyanine or a metal-free phthalocyanine or combination thereof, and a metal of the metal phthalocyanine is any one of Ca, Ba, Cd, Na, Cu, Ni, Co, Fe, Mg, Zn, Al, Mn, V, Ti, and Sn.

[0010]

According to the invention of (2), the effect of maintaining the corrosion resistance and weather resistance of the coating film to be formed can be more preferably obtained, and the preferable designability imparted to the metal surface can be maintained.

[0011]

(3) The aqueous coating agent for a steel material according to (1) or (2), in which a 20°C viscosity of the aqueous coating agent for a steel material is 100 mPa·s or less.

[0012]

According to the invention of (3), the aqueous coating agent for a steel material can obtain preferable coatability, coating unevenness can be eliminated, and preferable designability can be imparted to a metal surface.

[0013]

(4) The aqueous coating agent for a steel material according to any one of (1) to (3), in which a mass ratio between the polyurethane resin particles (A-1) and the ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) is (A-1):(A-2) = 20:80 to 90:10.

[0014]

According to the invention of (4), a coating film having excellent solvent resistance and alkali resistance can be formed.

[0015]

(5) The aqueous coating agent for a steel material according to any one of (1) to (4), further including: silicon oxide particles (E) having a mode size of 70 to 200 nm.

[0016]

According to the invention of (5), a hardness of the coating film to be formed can be improved, and a friction coefficient can be adjusted to a suitable range.

Therefore, abrasion resistance of the coating film can be improved.

[0017]

(6) A coating film formed of the aqueous coating agent for a steel material according to any one of (1) to (5) and having a chroma C^* of 2.0 or more and 50 or less.

[0018]

According to the invention of (6), preferable designability can be imparted to a steel material by the coating film formed of the aqueous coating agent for a steel material.

[0019]

(7) A method of coating a steel material, including: applying the aqueous coating agent for a steel material according to any one of (1) to (5) onto a surface of a steel material to form a coating film.

[0020]

According to the invention of (7), it is possible to form a coating film capable of maintaining corrosion resistance and weather resistance on the surface of the steel material and imparting preferable designability to a metal surface.

[0021]

(8) A steel material having a surface on which a coating film is formed of the aqueous coating agent for a steel material according to any one of (1) to (5), and having a 60° glossiness of 50% or more.

[0022]

According to the invention of (8), it is possible to provide a steel material to which preferable designability is imparted.

[0023]

(9) The steel material according to (8), in which the steel material is any one of a hot-dip galvanized steel and an aluminum-containing galvanized steel.

[0024]

According to the invention of (9), it is possible to provide a steel material to which preferable designability is imparted.

[Embodiments of the Invention]

[0025]

Hereinafter, embodiments of the present invention will be described. The present invention is not limited to the following embodiments.

[0026]

<Aqueous Coating Agent for Steel Material>

An aqueous coating agent for a steel material according to the present embodiment includes polyurethane resin particles (A-1) (hereinafter, sometimes simply referred to as “resin particles (A-1)”) and ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) (hereinafter, sometimes simply referred to as “resin particles (A-2)”), silicon oxide particles (B), an organic titanium compound (C), and a phthalocyanine pigment (F). In addition, wax particles (D) and silicon oxide particles (E) may be included.

[0027]

The polyurethane resin particles (A-1) have a median diameter of 20 to 100 nm and have a silanol group or an alkoxysilyl group or combination thereof. The resin particles (A-1) are not particularly limited, but for example, a polycarbonate-based polyurethane is preferable in that excellent solvent resistance and alkali resistance are provided. The polycarbonate-based polyurethane resin particles can be

obtained, for example, by the following method. First, a polyurethane prepolymer is manufactured by reacting an isocyanate group-containing compound, a polycarbonate polyol, a low molecular weight polyol, and a compound having an active hydrogen group and a hydrophilic group with each other. Next, the hydrophilic group is neutralized with a neutralizing agent. Next, the neutralized prepolymer that is neutralized is dispersed in water containing alkoxysilanes containing an active hydrogen group and amines for chain extension, thereby obtaining polycarbonate-based polyurethane resin particles having a silanol group or an alkoxysilyl group or combination thereof.

[0028]

The isocyanate group-containing compound is not particularly limited, and examples thereof include aliphatic diisocyanates such as hexamethylene diisocyanate, alicyclic diisocyanates such as 1,3-cyclohexane diisocyanate, isophorone diisocyanate, 4,4-methylenebis(cyclohexyl isocyanate), methyl-2,4-cyclohexane diisocyanate, methyl-2,6-cyclohexane diisocyanate, and 1,3-bis(isocyanatomethyl)cyclohexane, aromatic diisocyanates such as m-phenylene diisocyanate, p-phenylene diisocyanate, 1,5-naphthalene diisocyanate, 4,4-diphenylmethane diisocyanate, 2,4- or 2,6-tolylene diisocyanate or mixtures thereof, and 4,4-toluidine diisocyanate.

[0029]

The polycarbonate polyol is not particularly limited, and examples thereof include those obtained by reacting one or two or more glycols selected from the group consisting of ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, bisphenol-A, and hydrogenated bisphenol-A with dimethyl carbonate, diphenyl

carbonate, ethylene carbonate, phosgene, or the like.

[0030]

The low molecular weight polyol is not particularly limited, and examples thereof include glycols such as ethylene glycol, propylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, 1,4-cyclohexanediol, and 1,4-cyclohexanedimethanol, glycerin, trimethylolpropane, and pentaerythritol.

[0031]

The compound having an active hydrogen group and a hydrophilic group is not particularly limited, and examples thereof include a sulfonic acid group-containing compound such as 2-hydroxyethanesulfonic acid or a derivative thereof, and a carboxy group-containing compound such as 2,2-dimethylolpropionic acid and 2,2-dimethylolbutyric acid or derivatives thereof. In the manufacturing of the polyurethane resin particles, these compounds may be used alone or in combination of two or more. The hydrophilic groups such as the carboxy group or the sulfonic acid group are preferably neutralized with a neutralizing agent in order to satisfactorily disperse the polyurethane prepolymer in water.

[0032]

The neutralizing agent is not particularly limited, and examples thereof include ammonia, tertiary amines such as triethylamine and dimethylethanolamine, and hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide. These may be used alone or in combination of two or more.

[0033]

The alkoxysilanes containing an active hydrogen group are not particularly limited, and examples thereof include amino group-containing silanes such as γ -(2-

aminoethyl)aminopropyltrimethoxysilane, γ -(2-aminoethyl)aminopropyltriethoxysilane, γ -(2-aminoethyl)aminopropylmethyldimethoxysilane, γ -(2-aminoethyl)aminopropylmethyldiethoxysilane, γ -aminopropyltrimethoxysilane, and γ -aminopropyltriethoxysilane, and mercapto group-containing silanes such as γ -mercaptopropyltrimethoxysilane, γ -mercaptopropylmethyldimethoxysilane, γ -mercaptopropyltriethoxysilane, and γ -mercaptopropylmethyldiethoxysilane.

[0034]

The amines used for the chain extension are not particularly limited, and examples thereof include diamines such as ethylenediamine, 1,2-propanediamine, 1,6-hexamethylenediamine, and piperazine, polyamines such as diethylenetriamine, dipropylenetriamine, and triethylenetetramine, and hydrazines. These may be used alone or in combination of two or more.

[0035]

The reaction for obtaining the polyurethane prepolymer from the isocyanate group-containing compound and the active hydrogen compound such as the polyol is preferably performed at a reaction temperature of, for example, 30°C to 100°C. The above reaction may be performed in the presence or absence of an organic solvent. As the organic solvent, an organic solvent having a relatively high solubility in water is preferable, and examples thereof include acetone, methyl ethyl ketone, acetonitrile, and N-methylpyrrolidone.

[0036]

A method of dispersing the neutralized prepolymer that is neutralized in water is not particularly limited, and examples thereof include a method using a homogenizer, a mixer, or the like. In this case, a temperature is preferably, for example, room temperature or higher and about 70°C or lower.

[0037]

In a case where an organic solvent is used in the reaction for obtaining the polyurethane prepolymer, the organic solvent may be distilled off under reduced pressure, if necessary.

[0038]

The ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) have a median diameter of 20 to 100 nm and have a silanol group or an alkoxy silyl group or combination thereof. The resin particles (A-2) are not particularly limited, and for example, resin particles obtained by reacting epoxy group-containing alkoxy silanes with a resin solution in which an ethylene-methacrylic acid copolymer resin is neutralized with an alkali metal hydroxide, ammonia, or an amine, or any combination thereof and is dispersed in water are preferable in that the resin particles are fine and can form a high-performance coating film.

[0039]

The ethylene-methacrylic acid copolymer resin is not particularly limited, and for example, preferably has an ethylene content of 70 to 90 mass% and a methacrylic acid content of 10 to 30 mass%. The ethylene-methacrylic acid copolymer resin may contain monomers other than ethylene and methacrylic acid, but an amount of the other monomers is preferably 10 mass% or less. A method of manufacturing the ethylene-methacrylic acid copolymer resin is not particularly limited, and for example, the ethylene-methacrylic acid copolymer can be manufactured by a known method such as polymerization using a high-pressure process low-density polyethylene manufacturing apparatus.

[0040]

The epoxy group-containing alkoxy silanes are not particularly limited, and

examples thereof include γ -glycidoxypentyltrimethoxysilane, γ -glycidoxypentylmethyldimethoxysilane, γ -glycidoxypentyltriethoxysilane, γ -glycidoxypentylmethyldiethoxysilane, and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane. These may be used alone or in combination of two or more.

[0041]

The epoxy group-containing alkoxysilanes are used preferably in an amount of 0.1 to 20 parts by mass, and more preferably in an amount of 1 to 10 parts by mass for the reaction with 100 parts by mass of a solid content of the water-dispersed ethylene-methacrylic acid copolymer resin. In a case where the epoxy group-containing alkoxysilanes are used in an amount of less than 0.1 parts by mass, alkali resistance of a coating film to be formed on a surface of a steel material and adhesion to a curable resin such as a lacquer decrease. Similarly, in a case where the epoxy group-containing alkoxysilanes are used in an amount of more than 20 parts by mass, there are cases where bath stability of the aqueous coating agent for a steel material decreases.

[0042]

A polyfunctional epoxy compound may be used in combination in the reaction of the water-dispersed ethylene-methacrylic acid copolymer resin with the epoxy group-containing alkoxysilanes. The polyfunctional epoxy compound is not particularly limited, and examples thereof include sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, propylene glycol diglycidyl ether, triglycidyl tris(2-hydroxyethyl) isocyanurate, bisphenol A diglycidyl ether, and hydrogenated bisphenol A diglycidyl ether. These may be used alone or in combination of two or more.

[0043]

The reaction of the water-dispersed ethylene-methacrylic acid copolymer resin with the epoxy group-containing alkoxysilanes and the polyfunctional epoxy compound is preferably performed under a temperature condition of 50°C to 100°C for 0.5 to 12 hours.

[0044]

A mass ratio between the resin particles (A-1) and the resin particles (A-2) is preferably (A-1):(A-2) = 20:80 to 90:10. In a case where an amount of the resin particles (A-1) is less than 20 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2), hydrophobicity of the coating film becomes high, and there are cases where tape peeling resistance decreases or solvent resistance to a highly hydrophobic solvent such as white gasoline decreases. In a case where the amount of the resin particles (A-1) exceeds 90 parts by mass, hydrophilicity of the coating film increases, and there are cases where a decrease in alkali resistance, a decrease in solvent resistance to a highly hydrophilic solvent such as ethanol, and deterioration of corrosion resistance of a worked portion due to the coating film becoming brittle occur.

[0045]

Since the resin particles (A-1) and the resin particles (A-2) have a silanol group or an alkoxysilyl group or combination thereof, a composite coating film is formed by a reaction with the silicon oxide particles (B) and the organic titanium compound (C). Accordingly, the solvent resistance, the alkali resistance, and the like of the coating film formed of the aqueous coating agent for a steel material can be improved.

[0046]

Particle sizes of the resin particles (A-1) and the resin particles (A-2) are both 20 to 100 nm. The particle size is a median diameter (D50) measured by a dynamic light scattering method. In a case where the particle size is less than 20 nm, coating workability decreases due to reasons such as a high viscosity of the aqueous coating agent for a steel material or a decrease in the bath stability. In a case where the particle size exceeds 100 nm, the tape peeling resistance and the solvent resistance of the coating film formed of the aqueous coating agent for a steel material decrease.

[0047]

The particle size of the resin particles (A-1) can be adjusted by changing an introduction amount of the hydrophilic functional group for obtaining water dispersibility, for example, a carboxy group or a sulfonic acid group, a kind or an amount of the neutralizing agent for neutralizing the hydrophilic functional group. The particle size of the resin particles (A-2) can be adjusted by changing a kind of neutralizing agent, water dispersion conditions, a kind or an amount of the epoxy group-containing alkoxysilanes, and a kind or an amount of the polyfunctional epoxy compound.

[0048]

The silicon oxide particles (B) have a particle size of 5 to 20 nm. The particle size is a mode size (most frequent particle size) measured by the dynamic light scattering method. When the particle size is in this range, light is transmitted, and thus preferable designability (gloss and chroma) can be obtained. The silicon oxide particles (B) are not particularly limited, and for example, colloidal silica and fumed silica can be used. Specific examples thereof include SNOWTEX-N, SNOWTEX-C (Nissan Chemical Corporation), ADELITE AT-20N, AT-20A (ADEKA Corporation), CATALOID S-20L, and CATALOID SA (JGC C&C). These may be used alone or in

combination of two or more.

[0049]

An amount of the silicon oxide particles (B) is preferably 5 to 100 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2), and is more preferably 10 to 50 parts by mass. In a case where the amount of the silicon oxide particles (B) is less than 5 parts by mass, there are cases where hardness and corrosion resistance of the coating film formed of the aqueous coating material for a steel material decrease. In a case where the amount of the silicon oxide particles (B) exceeds 100 parts by mass, there are cases where film forming properties and water resistance of the coating film decrease.

[0050]

The organic titanium compound (C) is not particularly limited, and examples thereof include dipropoxybis(triethanolaminato)titanium, dipropoxybis(diethanolaminato)titanium, dibutoxybis(triethanolaminato)titanium, dibutoxybis(diethanolaminato)titanium, dipropoxybis(acetylacetonato)titanium, dibutoxybis(acetylacetonato)titanium, dihydroxybis(lactato)titanium monoammonium salt, dihydroxybis(lactato)titanium diammonium salt, propanedioxytitaniumbis(ethylacetoacetate), and oxotitaniumbis(monoammonium oxalate). These may be used alone or in combination of two or more.

[0051]

An amount of the organic titanium compound (C) is preferably 0.05 to 3 parts by mass, and more preferably 0.1 to 2 parts by mass in terms of titanium atoms with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the organic titanium compound (C) is less than 0.05 parts by mass, combination of components in the coating film formed of the

aqueous coating agent for a steel material becomes insufficient, and there are cases where the performance of the coating film decreases. In a case where the amount of the organic titanium compound (C) exceeds 3 parts by mass, there are cases where the hydrophilicity of the coating film becomes excessively high, the performance of the coating film decreases, and the bath stability of the aqueous coating agent for a steel material decreases.

[0052]

The wax particles (D) may be added in order to reduce a kinetic friction coefficient of the coating film formed of the aqueous coating agent for a steel material and to improve lubricity of a surface of the coating film. In this case, it is preferable that the wax particles (D) has a particle size of 0.5 to 4 μm and a softening point is 100°C to 140°C. The wax particles (D) are not particularly limited, and polyolefin wax particles (D) are preferable from the viewpoint (gloss and chroma) of improving the designability. The polyolefin wax particles (D) are not particularly limited, and examples thereof include hydrocarbon-based waxes such as paraffin, microcrystalline, and polyethylene, and derivatives thereof. The derivatives are not particularly limited, and examples thereof include carboxylated polyolefins and chlorinated polyolefins.

[0053]

In a case where the wax particles (D) are added to the aqueous coating agent for a steel material, the particle size is not particularly limited, and is preferably 0.5 to 4 μm . The particle size is a median diameter (D50) measured by a dynamic light scattering method. In a case where the particle size is less than 0.5 μm , there are cases where the lubricity of the formed coating film is insufficient. In a case where the particle size exceeds 4 μm , there is a possibility that problems such as non-uniform distribution of the wax particles (D) and loss from the coating film occur.

[0054]

In the aqueous coating agent for a steel material according to the present embodiment, in addition to the silicon oxide particles (B) having a particle size (mode size) of 5 to 20 nm, the silicon oxide particles (E) having a particle size (mode size) of 70 to 200 nm may be contained. The particle size is a mode size (most frequent particle size) measured by the dynamic light scattering method. When the silicon oxide particles (E) are contained in the aqueous coating agent for a steel material, hardness of the coating film can be improved and a friction coefficient can be adjusted to a suitable range. Therefore, abrasion resistance of the coating film is improved, so that a coil collapse of a coated steel sheet on which the coating film is formed, a load collapse of a cut sheet, and the like can be prevented, thereby improving a handling property of a steel material with the coating film.

[0055]

When the particle size of the silicon oxide particles (E) is set to 70 nm or more, the hardness and the friction coefficient of the coating film can be improved. In addition, when the particle size is set to 200 nm or less, the silicon oxide particles (E) are less likely to settle in the aqueous coating agent for a steel material, and dispersibility can be secured.

[0056]

The silicon oxide particles (E) have a larger particle size (mode size) than the silicon oxide particles (B). The silicon oxide particles (E) are not particularly limited, and known silicon oxide particles can be used. Examples thereof include ST-ZL, MP-1040 (manufactured by Nissan Chemical Corporation), PL-7 (manufactured by FUSO CHEMICAL Co., Ltd.), and SI-80P (manufactured by JGC C&C). These may be used alone or in combination of two or more.

[0057]

An amount of the silicon oxide particles (E) is preferably 1 to 20 parts by mass, and more preferably 1 to 10 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the silicon oxide particles (E) is less than 1 part by mass, it is difficult to obtain the effect of adjusting the friction coefficient. Therefore, the silicon oxide particles (E) may be contained in an amount of 1 part by mass or more. In addition, when the amount of the silicon oxide particles (E) exceeds 20 parts by mass, there is a concern that a film-forming property and water resistance of the coating film decreases.

[0058]

The phthalocyanine pigment (F) imparts a preferable chroma C^* to the formed coating film while maintaining glossiness of the coated steel material. A phthalocyanine in the phthalocyanine pigment (F) is preferably a metal phthalocyanine or a metal-free phthalocyanine or combination thereof. As a metal of the metal phthalocyanine, for example, any one of Ca, Ba, Cd, Na, Cu, Ni, Co, Fe, Mg, Zn, Al, Mn, V, Ti, and Sn is preferable. The phthalocyanine is more preferably a metal phthalocyanine in which the metal is either Cu or Sn. A crystal structure of the phthalocyanine is not particularly limited, and a generally used α -type or β -type phthalocyanine may be used, or a phthalocyanine having any other crystal structure may be used.

[0059]

A method of obtaining the phthalocyanine is not particularly limited. For example, as a method of obtaining copper phthalocyanine, there are known methods such as a urea method (Wyler method), in which phthalic acid or a derivative thereof and urea or a derivative thereof are heated and reacted in an organic solvent in the

presence of a copper compound and a catalyst, and a phthalodinitrile method in which phthalodinitrile is heated and reacted in an organic solvent in the presence of a copper compound.

[0060]

Since the phthalocyanine obtained by the above-described production method forms aggregates of fine pigments, using a known method as a refinement method, such as an acid pasting method and a solvent salt milling method, phthalocyanine particles having a very small primary particle size, a narrow width distribution, and a sharp particle size distribution can be obtained. In addition, in order to prevent the reaggregation of the phthalocyanine particles, a resin and/or a surfactant may be added. A phthalocyanine dispersion can be obtained by coating.

[0061]

A method of coating the phthalocyanine with the resin or the surfactant is not particularly limited. For example, in the solvent salt milling method, by kneading the phthalocyanine, the resin and/or the surfactant, a water soluble inorganic salt, and a water soluble organic solvent using an extruder or the like, the phthalocyanine can be refined, and a surface of the phthalocyanine can be uniformly coated with the resin or the surfactant. When the phthalocyanine is refined by a method other than the above method, a resin and/or a surfactant may be added to coat the surface of the phthalocyanine, or a resin and/or a surfactant may be added after the refinement to coat the surface of the phthalocyanine. Accordingly, preferable dispersibility of the phthalocyanine (F) in the aqueous coating agent for a steel material is obtained, and as a result, the coating film formed of the aqueous coating agent for a steel material and the steel material coated with the coating film can obtain a preferable chroma and gloss.

[0062]

The resin has a pigment-affinitive portion having a property of adsorbing to a pigment and a portion compatible with a colorant carrier, and has a function of adsorbing to the pigment and stabilizing dispersion of the pigment in the colorant carrier. The resin is not particularly limited, and natural resins, modified natural resins, synthetic resins such as acrylic resins, synthetic resins modified with natural resins, and the like can be used. As the natural resin, rosin is representative, and as the modified natural resin, a rosin derivative, a cellulose derivative, a rubber derivative, a protein derivative, and an oligomer thereof are used. Examples of the synthetic resin include an epoxy resin, an acrylic resin, a maleic acid resin, a butyral resin, a polyester resin, a melamine resin, a phenol resin, a polyurethane resin, and a polyamide resin. Examples of the synthetic resin modified with a natural resin include a rosin-modified maleic acid resin, a rosin-modified fumaric acid resin, and a rosin-modified phenol resin.

[0063]

Specific examples include polycarboxylic acid esters such as polyurethanes and polyacrylates, unsaturated polyamides, polycarboxylic acids, polycarboxylic acid (partial) amine salts, polycarboxylic acid ammonium salts, polycarboxylic acid alkylamine salts, polysiloxanes, long-chain polyaminoamide phosphates, hydroxyl group-containing polycarboxylic acid esters, modified products thereof, oil-based dispersants such as amides formed by a reaction of poly(lower alkyleneimine) with polyesters having free carboxyl groups and salts thereof, water soluble resins or water soluble polymer compounds such as (meth)acrylic acid-styrene copolymers, (meth)acrylic acid-(meth)acrylic acid ester copolymers, styrene-maleic acid copolymers, polyvinyl alcohol, and polyvinylpyrrolidone, polyesters, modified polyacrylates, ethylene oxide/propylene oxide adducts, and phosphate esters, and these

can be used alone or in combination of two or more.

[0064]

The surfactant is not particularly limited, and hitherto known anionic surfactants, nonionic surfactants, cationic surfactants, amphoteric surfactants, and the like can be used.

[0065]

Specifically, examples of the anionic surfactant include sodium lauryl sulfate, polyoxyethylene alkyl ether sulfate, sodium dodecylbenzenesulfonate, alkali salts of styrene-acrylic acid copolymers, sodium stearate, sodium alkylnaphthalenesulfonate, sodium alkyldiphenyl ether disulfonate, monoethanolamine lauryl sulfate, triethanolamine lauryl sulfate, ammonium lauryl sulfate, monoethanolamine stearate, sodium stearate, sodium lauryl sulfate, monoethanolamines of styrene-acrylic acid copolymers, and polyoxyethylene alkyl ether phosphate. Examples of the nonionic surfactant include polyoxyethylene oleyl ether, polyoxyethylene lauryl ether, polyoxyethylene nonylphenyl ether, polyoxyethylene alkyl ether phosphate, polyoxyethylene sorbitan monostearate, polyethylene glycol monolaurate, acetylene glycol, and polyoxyethylene acetylene glycol. Examples of the chaotic surfactant include an alkyl quaternary ammonium salt and an ethylene oxide adduct thereof. Examples of the amphoteric surfactant include an alkyl betaine such as an alkyl dimethylaminoacetic acid betaine and an alkyl imidazoline. These can be used alone or in combination of two or more.

[0066]

An amount of the phthalocyanine pigment (F) is 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). The amount of the phthalocyanine pigment (F) is preferably 0.05 to 5 parts by

mass. In a case where the amount of the phthalocyanine pigment (F) is less than 0.01 parts by mass, there are cases where the formed coating film cannot obtain a preferable chroma. In a case where the amount of the phthalocyanine pigment (F) exceeds 10 parts by mass, there are cases where the glossiness of the steel material on which the coating film is formed decreases.

[0067]

A particle size of the phthalocyanine pigment (F) is 0.01 to 1.0 μm . The particle size is a primary particle size measured by an electron microscope. The primary particle size is preferably 0.05 to 1.0 μm . In a case where the primary particle size of the phthalocyanine pigment (F) is less than 0.01 μm , there are cases where preferable dispersibility in the aqueous coating agent for a steel material cannot be obtained, and chroma and gloss cannot be obtained. In a case where the primary particle size exceeds 1.0 μm , diffuse reflection of light occurs in the coating film, and there are cases where the coating film cannot obtain a preferable chroma. In addition, there are cases where the steel material on which the coating film is formed cannot obtain a preferable glossiness.

[0068]

The aqueous coating agent for a steel material according to the present embodiment further preferably contains at least one antirust agent selected from the group consisting of a phosphate compound, a thiocarbonyl compound, a niobium oxide, and a guanidine compound. Accordingly, the steel material on which the coating film is formed can obtain excellent corrosion resistance.

[0069]

Examples of the phosphate compound include phosphoric acids such as orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, triphosphoric acid,

and tetraphosphoric acid, and phosphates such as triammonium phosphate, diammonium hydrogen phosphate, trisodium phosphate, and disodium hydrogen phosphate. These may be used alone or in combination of two or more. By using the above phosphate compound, phosphate ions form a phosphate layer on the surface of the steel material for passivation, thereby improving antirust properties of the steel material.

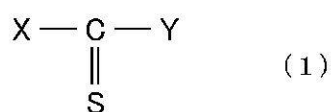
[0070]

An amount of the phosphate compound is preferably 0.01 to 5 parts by mass, and more preferably 0.05 to 3 parts by mass in terms of phosphate ions with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the phosphate compound is less than 0.01 parts by mass, the corrosion resistance is insufficient. When the amount of the phosphate compound exceeds 5 parts by mass, there are cases where gelation occurs depending on an aqueous dispersion resin and coating cannot be performed.

[0071]

The thiocarbonyl compound, niobium oxide, and guanidine compound are particularly effective in preventing white rust on a zinc steel material and the like, like chromium compounds that have been hitherto used to impart corrosion resistance. The thiocarbonyl compound is a compound having a thiocarbonyl group and is, for example, represented by General Formula (1).

[0072]



[0073]

In Formula (1), X and Y represent H, OH, SH, NH₂, one having OH, SH, or NH₂ as a substituent, or a hydrocarbon group having 1 to 15 carbon atoms and having -O-, -NH-, -S-, -CO-, or -CS- as a substituent. X and Y may be bonded to each other to form a ring. The thiocarbonyl compound represented by Formula (1) preferably has a nitrogen atom or an oxygen atom.

[0074]

In addition to the above, as the thiocarbonyl compound, a compound capable of forming a thiocarbonyl group-containing compound in an aqueous solution or in the presence of an acid or an alkali may be used. Examples thereof include thiourea and derivatives thereof such as methylthiourea, dimethylthiourea, trimethylthiourea, ethylthiourea, diethylthiourea, 1,3-dibutylthiourea, phenylthiourea, diphenylthiourea, 1,3-bis(dimethylaminopropyl)-2-thiourea, ethylenethiourea, and propylenethiourea.

[0075]

In addition to the above, as the thiocarbonyl compound, carbothioic acids and salts thereof may be used. Examples thereof include thioacetic acid, thiobenzoic acid, dithioacetic acid, sodium methylthiocarbamate, sodium dimethylthiocarbamate, triethylamine dimethylthiocarbamate, sodium diethylthiocarbamate, pentamethylenedithiocarbamate piperidine salt, pipecholyldithiocarbamate pipercoline salt, and potassium o-ethylxanthate.

[0076]

These thiocarbonyl compounds may be used alone or in combination of two or more. In addition, among the above-mentioned thiocarbonyl compounds, those having low solubility in water can be dissolved in a solvent such as an alkaline solution and then blended in the aqueous coating agent for a steel material.

[0077]

An amount of the thiocarbonyl compound is preferably 0.1 to 10 parts by mass, and more preferably 0.2 to 5 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the thiocarbonyl compound is less than 0.1 part by mass, the corrosion resistance is insufficient. When the amount of the thiocarbonyl compound exceeds 10 parts by mass, the corrosion resistance is saturated, which is uneconomical, and there are cases where gelation occurs depending on an aqueous dispersion resin used, making coating impossible.

[0078]

The niobium oxide is preferably niobium oxide colloidal particles. Accordingly, the corrosion resistance of the formed coating film can be further improved. The niobium oxide colloidal particles preferably have a particle size of 100 nm or less from the viewpoint of more stably forming a dense niobium oxide-containing coating film and stably imparting antirust properties to an object to be treated. The particle size is a mode size (most frequent particle size) measured by the dynamic light scattering method. The particle size is more preferably 2 to 50 nm, and even more preferably 2 to 20 nm.

[0079]

The niobium oxide colloidal particles indicate that niobium oxide is dispersed in water in a state of fine particles. The niobium oxide includes, for example, those in an amorphous state in an intermediate state between niobium hydroxide and niobium oxide in which niobium oxide is not strictly formed. The niobium oxide colloidal particles are not particularly limited, and a niobium oxide sol manufactured by a known method can be used.

[0080]

An amount of the niobium oxide is preferably 0.1 to 5 parts by mass, and more preferably 0.2 to 3 parts by mass in terms of Nb_2O_5 with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the niobium oxide is less than 0.1 parts by mass, sufficient antirust properties cannot be obtained, which is not preferable. Even if the amount of the niobium oxide exceeds 5 mass%, no improvement in the effect is observed, which is not economical.

[0081]

The guanidine compound is not particularly limited, and examples thereof include guanidine, aminoguanidine, guanylthiourea, 1,3-di-o-tolylguanidine, 1-o-tolylbiguanide, and 1,3-diphenylguanidine. The guanidine compound may be used alone or in combination of two or more.

[0082]

An amount of the guanidine compound is preferably 0.1 to 5 parts by mass, and more preferably 0.2 to 3 parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2). In a case where the amount of the guanidine compound is less than 0.1 parts by mass, the corrosion resistance is insufficient. When the amount of the guanidine compound exceeds 5 parts by mass, the corrosion resistance is saturated, which is uneconomical, and there are cases where gelation occurs depending on an aqueous dispersion resin used, making coating impossible.

[0083]

The aqueous coating agent for a steel material according to the present embodiment may contain components other than the above as long as the effects of the present invention are not impaired. For example, a defoaming agent, an organic

solvent, and a leveling agent may be contained. The organic solvent is not particularly limited as long as the organic solvent is generally used for a lacquer, and examples thereof include alcohol-based, ketone-based, ester-based, and ether-based hydrophilic solvents. The leveling agent is not particularly limited, and examples thereof include silicone-based and fluorine-based leveling agents.

[0084]

As the solvent of the aqueous coating agent for a steel material according to the present embodiment, water, a mixture of water and various alcohols, and the like can be used.

[0085]

The aqueous coating agent for a steel material according to the present embodiment preferably has a viscosity at 20°C of 100 mPa·s or less. In a case where the viscosity at 20°C exceeds 100 mPa·s, for example, during coating, the coating agent transferred from a coating roll to an object to be coated tends to form string-like droplets, and uneven coating tends to occur. The viscosity of the aqueous coating agent for a steel material is more preferably 50 mPa·s or less. A lower limit of the viscosity of the aqueous coating agent for a steel material is not particularly limited, and may be, for example, 3 mPa·s or more or 5 mPa·s or more.

[0086]

<Coating Film Formed of Aqueous Coating Agent for Steel Material>

The coating film formed of the aqueous coating agent for a steel material according to the present embodiment (hereinafter, sometimes simply referred to as “coating film”) is made of a composite resin in which the above components are composited. That is, the composite resin is a state in which the functional groups of the components form bonds and are combined. The bond is a bond formed by a

reaction of a Si-OH group or a Si-OR group or combination thereof of the resin particles (A-1) and (A-2) with a Si-OH group of surfaces of the silicon oxide particles (B) and (E) or Ti-OH and Ti-OR' groups of the organic titanium compound (C) or combination thereof, and the like. The bond is considered to be, for example, a Si-O-Si bond or a Si-O-Ti-O-Si bond, and organic resin particles and inorganic particles form a chemically strong bond.

[0087]

The coating film of the present embodiment is a coating film that contains the resin containing the polyurethane resin particles and the ethylene-unsaturated carboxylic acid copolymer resin particles, the silicon oxide particles, Ti, and the phthalocyanine pigment, in which the amount of the phthalocyanine pigment is 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the polyurethane resin particles and the ethylene-unsaturated carboxylic acid copolymer resin particles and the particle size (primary particle size) of the phthalocyanine pigment is 0.01 to 1.0 μm . There are cases where the silicon oxide particles include silicon oxide particles having a particle size (mode size) of 5 to 20 nm, and further include silicon oxide particles having a particle size (mode size) of 70 to 200 nm. Ti is derived from the organic titanium compound (C). That is, the coating film of the present embodiment contains Ti as an element. In addition, inclusion of the phthalocyanine pigment can be confirmed by confirming inclusion of phthalocyanine in the coating film. Furthermore, the coating film may contain the above-mentioned antirust agent or other additive components.

[0088]

The coating film has a chroma C^* of 2.0 or more and 50 or less. When the chroma C^* of the coating film is 2.0 or more, the coating film exhibits a clear color

tone and a good color developing property, which is preferable. The chroma C^* is more preferably 5.0 or more. In addition, the chroma C^* is set to 50 or less. The chroma C^* is more preferably less than 50. In a case where the chroma C^* is less than 2.0, there is a possibility that the color developing property of the coating film is poor. The chroma C^* can be measured using a commercially available color difference meter, for example, a spectrophotometer SE6000 manufactured by NIPPON DENSHOKU INDUSTRIES Co., LTD. The chroma C^* is calculated by the following formula. In the following formula, regarding a^* and b^* , in an $L^*a^*b^*$ color system, a^* indicates a color in a red direction, $-a^*$ indicates a color in a green direction, b^* indicates a color in a yellow direction, and $-b^*$ indicates a color in a blue direction.

[0089]

[Formula 1]

$$\text{Chroma : } (C^*) = \sqrt{(a^*)^2 + (b^*)^2}$$

[0090]

A coating amount of the coating film is preferably 0.5 to 3 g/m², and more preferably 0.5 to 2 g/m². When the coating amount is less than 0.5 g/m², there are cases where the corrosion resistance and the alkali resistance decrease. On the other hand, when the coating amount is too large, not only is adhesion to a substrate reduced, but also the large coating amount is uneconomical.

[0091]

<Method of Coating Steel Material>

[0092]

A method of coating a steel material is to apply the above-mentioned aqueous

coating agent for a steel material to a metal surface to form a coating film, and includes a coating step and a heat curing step.

[0093]

In the coating step, the above-mentioned aqueous coating agent for a steel material is uniformly applied to a metal surface. A coating method is not particularly limited, and generally used roll coatings, air sprays, airless sprays, immersions, and the like can be appropriately adopted. In order to enhance curability of the coating film, the steel material to be coated may be heated in advance.

[0094]

In the heat curing step, the steel material to which the aqueous coating agent for a steel material is applied is heated to form a coating film on the surface of the steel materials. A heating temperature of the steel material to be coated is 50°C to 250°C, and preferably 70°C to 220°C. When the heating temperature is lower than 50°C, an evaporation rate of water is slow and sufficient film forming properties cannot be obtained, so that the solvent resistance and the alkali resistance decrease. On the other hand, when the heating temperature exceeds 250°C, the resin is thermally decomposed, physical properties of the coating film are deteriorated, causing deterioration of various performances, and deterioration of an external appearance, such as yellowing. A heat curing time is preferably 1 second to 5 minutes.

[0095]

In addition to the above, the method of coating a steel material may include an overcoating applying step of applying an overcoating on the coating film. Examples of the overcoating lacquer used in the overcoating applying step include lacquers made of an acrylic resin, an acrylic-modified alkyd resin, an epoxy resin, a urethane resin, a melamine resin, a phthalic acid resin, an amino resin, a polyester resin, and a vinyl

chloride resin. A film thickness of a coating film of the overcoating lacquer is appropriately determined depending on an intended use of an antirust metal product, a type of the overcoating lacquer to be used, and the like, and is not particularly limited. Usually, the film thickness is about 5 to 300 μm , and more preferably about 10 to 200 μm . The coating film of the overcoating lacquer can be formed by applying the overcoating lacquer onto the coating film formed of the aqueous coating agent for a steel material, and heating, drying, and curing the overcoating lacquer. A heating temperature can be set to, for example, 50°C to 250°C, and a heating time can be set to 5 minutes to 1 hour.

[0096]

<Steel Material Coated with Aqueous Coating Material for Steel Material>

A steel material according to the present embodiment includes a steel material (substrate), a plating layer disposed on the steel material (substrate), and a coating film disposed on a surface of the plating layer. As described above, the coating film includes the resin containing the polyurethane resin particles and the ethylene-unsaturated carboxylic acid copolymer resin particles, the silicon oxide particles, Ti, and the phthalocyanine pigment. The amount of the phthalocyanine pigment is 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the polyurethane resin particles and the ethylene-unsaturated carboxylic acid copolymer resin particles. The primary particle size of the phthalocyanine pigment is 0.01 to 1.0 μm .

[0097]

The steel material in which the coating film is formed on the surface by the aqueous coating agent for a steel material according to the present embodiment is not particularly limited, and examples thereof include zinc-based plated steel materials such as an aluminum-containing galvanized steel material, a galvanized steel material,

a zinc-nickel plated steel material, a zinc-iron plated steel material, a zinc-chromium plated steel material, a zinc-titanium plated steel material, a zinc-magnesium plated steel material, a zinc-manganese plated steel material, a zinc-aluminum-magnesium plated steel material, and a zinc-aluminum-magnesium-silicon plated steel material, those containing, as a small amount of dissimilar metal elements or impurities, cobalt, molybdenum, tungsten, nickel, titanium, chromium, aluminum, manganese, iron, magnesium, lead, bismuth, antimony, tin, copper, cadmium, and arsenic in plating layers thereof, and those in which an inorganic substance such as silica, alumina, or titania is dispersed. Furthermore, the steel material can also be applied to a multi-layer plating in which the above plating and other types of plating, such as iron plating, iron-phosphorus plating, nickel plating, and cobalt plating, are combined. Moreover, the steel material can also be applied to aluminum or aluminum-based alloy plating. A plating method is not particularly limited, and may be any known method such as an electro plating method, a hot-dip plating method, a vapor deposition plating method, a dispersion plating method, or a vacuum plating method. As the steel material, the aluminum-containing galvanized steel material is preferable.

[0098]

The steel material having the coating film formed on the surface according to the present embodiment preferably has a 60° glossiness of 50% or more. The 60° glossiness is more preferably 50% to 200%, and even more preferably 60% to 150%. In a case where the 60° glossiness is less than 50%, the steel material cannot obtain a preferable external appearance. In addition, a more preferable 60° glossiness is set to 200% or less from an upper limit of a 60° glossiness of a general plated steel material. However, by applying a special manufacturing method, post-manufacturing polishing, or the like to the steel material, the 60° glossiness can exceed 200%, and may exceed

200%. The 60° glossiness can be measured based on a method specified in JIS Z 8741, and can be measured using, for example, a commercially available gloss meter (VG2000 manufactured by NIPPON DENSHOKU INDUSTRIES Co., LTD).

[0099]

The steel material having the coating film formed on the surface according to the present embodiment has preferable glossiness and chroma while maintaining corrosion resistance and accelerated weather resistance, and thus obtains an external appearance having excellent designability.

[Examples]

[0100]

Hereinafter, the contents of the present invention will be described in more detail based on examples. The contents of the present invention are not limited to the description of the following examples.

[0101]

<Manufacturing of Aqueous Dispersion Liquid of Resin Particles (A-1)>

(Manufacturing Example 1)

Into a reaction container, 4,4-methylenebis(cyclohexyl isocyanate), polycarbonatediol having a molecular weight of 2000, neopentyl glycol, dimethylolpropionic acid, and N-methylpyrrolidone as a solvent are put, stirred at 80°C for 6 hours, and then neutralized with dimethylethanolamine, thereby obtaining a polyurethane prepolymer solution. Next, the polyurethane prepolymer solution obtained by the above reaction was dispersed in water containing hydrazine and γ -(2-aminoethyl)aminopropyltriethoxysilane using a homodisper, thereby obtaining an aqueous dispersion liquid of polycarbonate-based polyurethane resin particles containing a silanol group and/or an ethoxysilyl group. A solid content concentration

thereof was 30 mass%, and a median diameter measured by the dynamic light scattering method was 39 nm.

[0102]

(Manufacturing Example 2)

The polyurethane prepolymer solution obtained by the above reaction in the same manner as in Manufacturing Example 1 was dispersed in water containing hydrazine and γ -(2-aminoethyl)aminopropylmethyldimethoxysilane using a homodisper, thereby obtaining an aqueous dispersion liquid of polycarbonate-based polyurethane resin particles containing a silanol group and/or an ethoxysilyl group. A solid content concentration thereof was 30 mass%, and a median diameter measured by the dynamic light scattering method was 20 nm.

[0103]

(Manufacturing Example 3)

Into a reaction container, 4,4-methylenebis(cyclohexyl isocyanate), dimethylolpropionic acid, and acetone were added and heated to 50°C while being stirred to be reacted with each other, and a polyester polyol having a molecular weight of 2000 obtained by a reaction of adipic acid, neopentyl glycol, and ethylene glycol was added and reacted to obtain a polyurethane prepolymer solution. Next, in water containing dimethylethanolamine, γ -(2-aminoethyl)aminopropyltriethoxysilane, and 2-(2-aminoethylamino)ethanol, the polyurethane prepolymer solution obtained by the above reaction was dispersed using a homodisper and heated to distill off acetone, thereby obtaining an aqueous dispersion liquid of polyester-based polyurethane resin particles containing a silanol group and/or an ethoxysilyl group. A solid content concentration thereof was 30 mass%, and a median diameter thereof was 32 nm.

[0104]

<Manufacturing of Aqueous Dispersion Liquid of Resin Particles (A-2)>

(Manufacturing Example 4)

Into a reaction container, an ethylene-methacrylic acid copolymer resin (a methacrylic acid content was 20 mass%), sodium hydroxide equivalent to 5.6 mass% with respect to the resin, and deionized water were added and stirred at 95°C for 6 hours, thereby obtaining an aqueous dispersion resin liquid having a solid content of 20 mass%. To this aqueous dispersion resin liquid, 0.8 mass% of γ -glycidoxypentyltrimethoxysilane and 0.8 mass% of glycerol polyglycidyl ether were further added and reacted at 85°C for 2 hours, thereby obtaining an aqueous dispersion liquid of ethylene-methacrylic acid copolymer resin particles having a silanol group and/or a methoxysilyl group. A solid content concentration thereof was 21 mass%, and a median diameter thereof was 50 nm.

[0105]

(Manufacturing Example 5)

Into a reaction container, an ethylene-methacrylic acid copolymer resin (a methacrylic acid content was 20 mass%), 3.7 mass% of sodium hydroxide with respect to the resin, 6.3 mass% of ammonia water, and deionized water were added and stirred at 95°C for 6 hours, thereby obtaining an aqueous dispersion resin liquid having a solid content of 20 mass%. To this aqueous dispersion resin liquid, 1.2 mass% of γ -glycidoxypentyltrimethoxysilane and 0.6 mass% of pentaerythritol polyglycidyl ether were further added and reacted at 85°C for 2 hours, thereby obtaining an aqueous dispersion liquid of ethylene-methacrylic acid copolymer resin particles having a silanol group and/or a methoxysilyl group. A solid content concentration thereof was 21 mass%, and a median diameter thereof was 100 nm.

[0106]

(Manufacturing Example 6)

Into a reaction container, an ethylene-methacrylic acid copolymer resin (a methacrylic acid content was 20 mass%), sodium hydroxide equivalent to 4.7 mass% with respect to the resin, and deionized water were added and stirred at 95°C for 2 hours, thereby obtaining an aqueous dispersion resin liquid having a solid content of 20 mass%. To this aqueous dispersion resin liquid, 1.2 mass% of γ -glycidoxypropyltrimethoxysilane and 1.2 mass% of hydrogenated bisphenol A diglycidyl ether were further added and reacted at 85°C for 2 hours, thereby obtaining an aqueous dispersion liquid of ethylene-methacrylic acid copolymer resin particles having a silanol group and/or a methoxysilyl group. A solid content concentration thereof was 21 mass%, and a median diameter thereof was 70 nm.

[0107]

(Manufacturing Example 7)

Into a reaction container, an ethylene-methacrylic acid copolymer resin (a methacrylic acid content was 20 mass%), 21.0 mass% of ammonia water with respect to the resin, and deionized water were added and stirred at 95°C for 2 hours, thereby obtaining an aqueous dispersion resin liquid having a solid content of 20 mass%. To this aqueous dispersion resin liquid, 1.2 mass% of γ -glycidoxypropyltrimethoxysilane and 1.2 mass% of hydrogenated bisphenol A diglycidyl ether were further added and reacted at 85°C for 2 hours, thereby obtaining an aqueous dispersion liquid of ethylene-methacrylic acid copolymer resin particles having a silanol group and/or a methoxysilyl group. A solid content concentration thereof was 21 mass%, and a median diameter thereof was 150 nm.

[0108]

(Manufacturing Example 8)

Into a reaction container, an ethylene-methacrylic acid copolymer resin (a methacrylic acid content was 27 mass%), 28.0 mass% of ammonia water with respect to the resin, and deionized water were added and stirred at 95°C for 2 hours, thereby obtaining an aqueous dispersion resin liquid having a solid content of 20 mass%. To this aqueous dispersion resin liquid, 1.6 mass% of γ -glycidoxypolytrimethoxysilane and 1.6 mass% of hydrogenated bisphenol A diglycidyl ether were further added and reacted at 85°C for 2 hours, thereby obtaining an aqueous dispersion liquid of ethylene-methacrylic acid copolymer resin particles having a silanol group and/or a methoxysilyl group. A solid content concentration thereof was 21 mass%, and a median diameter thereof was 14 nm.

[0109]

(Manufacturing Example 9)

Into a reaction container, 190 parts by mass of a bisphenol F epichlorohydrin type epoxy resin with an epoxy equivalent amount of 190, 30 parts by mass of diethanolamine, and 110 parts by mass of propylene glycol monomethyl ether acetate were added and reacted at 100°C for 2 hours, thereby obtaining a modified epoxy resin having a solid content concentration of 70%. Into a reaction container, 100 parts by mass of a 2,4-toluene diisocyanate prepolymer of trimethylolpropane with an NCO content of 13.3% and a non-volatile content of 75%, 44 parts by mass of nonylphenol, 5 parts by mass of dimethylbenzylamine, and 65 parts by mass of propylene glycol monomethyl ether acetate were mixed and reacted at 80°C for 3 hours in a nitrogen atmosphere, thereby obtaining a half-blocked polyisocyanate having a solid content concentration of 70% and an NCO% of 20%. After 70 parts by mass of the modified epoxy resin and 30 parts by mass of the half-blocked polyisocyanate were mixed and stirred at 80°C for 4 hours to react with each other, it was confirmed by infrared

spectroscopy that absorption of NCO groups was completely eliminated. Thereafter, the resultant was diluted with ion exchange water to obtain an aqueous epoxy resin. A solid content concentration thereof was 25 mass%, and a median diameter thereof was 600 nm.

[0110]

<Preparation of Aqueous Coating Agent for Steel Material According to Examples and Comparative Examples>

(Example 1)

80 parts by mass of the aqueous dispersion liquid of the resin particles (A-1) of Manufacturing Example 1 in terms of solid content and 20 parts by mass of the aqueous dispersion liquid of the resin particles (A-2) of Manufacturing Example 4 in terms of solid content were used. As the silicon oxide particles (B), silicon oxide particles having a particle size (mode size) of 15 nm were used. As the organic titanium compound (C), dipropoxybis(triethanolaminate)titanium was used. As the wax particles (D), polyethylene particles having a particle size (median diameter) of 1.0 μm and a softening point of 115°C were used. As the silicon oxide particles (E), silicon oxide particles having a particle size (mode size) of 100 nm were used. As the phthalocyanine pigment (F), Cu phthalocyanine (primary particle size 0.26 μm) using a surfactant as a coating agent was used. As the antirust agent (G), phosphate and thiourea were used. The amount of each component is parts by mass with respect to a total of 100 parts by mass of the resin particles (A-1) and the resin particles (A-2), and a coating adjusting agent for a steel material according to Example 1 was prepared using the amounts shown in Table 6. The amount of the organic titanium compound (C) shown in Table 6 is parts by mass in terms of titanium atoms.

[0111]

(Examples 2 to 18 and Comparative Examples 1 to 21)

Coating adjusting agents for a steel material according to Examples 2 to 18 and Comparative Examples 1 to 20 were each prepared in the same manner as in Example 1 except that the raw materials shown in Table 6 were used. In addition, Comparative Example 12 was adjusted to have a high viscosity through aging at 60°C and used as Comparative Example 21. Correspondence between the types of the silicon oxide particles (B), the organic titanium compound (C), the silicon oxide particles (E), the phthalocyanine pigment (F), and the antirust agent (G) shown in Table 6 and the symbols shown in Table 6 is shown in Tables 1 to 5 below.

[0112]

Details of the phthalocyanine pigment (F) shown in Table 4 are as follows.

Type k: “SA Blue 5204” manufactured by Mikuni-Color Ltd.

Type l: “LIOFAST SF670 Blue” manufactured by Toyocolor Co., Ltd.

Type m: “SA Blue 5205” manufactured by Mikuni-Color Ltd.

Kind n: “DP Color 1737 Blue” manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

Type o: “DP Color 1534 Blue” manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

Type p: “DP-1957 Yellow” manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

Type q: “NAF Color NAF1032 Red” manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

Type r: “LIOFAST BLUE G227” manufactured by Toyocolor Co., Ltd.

Type s: “EMF BLUE HG” manufactured by Toyocolor Co., Ltd.

Type t: “PSM Sky Blue FG” manufactured by Mikuni-Color Ltd.

Type u: “TB Color TB-700 BlueGA” manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

[0113]

[Table 1]

Type	Substance name	Mode size (nm)
a	Silicon oxide particles	15
b	Silicon oxide particles	5
c	Silicon oxide particles	20
d	Silicon oxide particles	2
e	Silicon oxide particles	40

[0114]

[Table 2]

Type	Substance name	Average particle size (nm)
f	Dipropoxybis(triethanolaminate)titanium	100
g	Dipropoxybis(acetylacetonate)titanium	70

[0115]

[Table 3]

Type	Substance name	Mode size (nm)
h	Silicon oxide particles	100
i	Silicon oxide particles	70
j	Silicon oxide particles	200

[0116]

[Table 4]

Type	Substance name	Coating agent	Primary particle size (μm)
k	Cu phthalocyanine	Surfactant	0.26
l	Cu phthalocyanine	Acrylic resin	0.36
m	Chlorinated Cu phthalocyanine	Acrylic resin	0.13
n	Cu phthalocyanine	Surfactant	1.91
o	Cu phthalocyanine	Surfactant	1.66
p	Disazo yellow	Acrylic resin	0.25
q	Quinacridone red	Acrylic resin	0.17
r	Cu phthalocyanine	Acrylic resin	0.01
s	Cu phthalocyanine	Surfactant	1.00
t	Chlorinated Cu phthalocyanine	Acrylic resin	0.003
u	Cu phthalocyanine	Surfactant	2.82

[0117]

[Table 5]

Type	Substance name
v	Phosphate
w	Thiourea
x	Sodium diethyldithiocarbamate
y	Niobium oxide
z	Guanylthiourea
aa	1-o-tolylbiguanide

[0118]

[Table 6]

	Composition																		Viscosity (mPa·s)
	A-1		A-2		B		C		D		E		F		G				
	Type	parts by mass	Type	parts by mass	Type	parts by mass	Type	parts by mass	Type	parts by mass	Type	Particle size (µm)	parts by mass	Type	parts by mass	Type	parts by mass		
Example 1	Manufacturing Example 1	80	Manufacturing Example 4	20	a	30	f	0.8	3	h	10	k	0.26	0.5	v	0.7	w	3.6	7
Example 2	Manufacturing Example 1	70	Manufacturing Example 4	30	a	30	f	0.8	-	h	5	l	0.36	2.5	v	1.2	y	1.3	7
Example 3	Manufacturing Example 3	70	Manufacturing Example 4	30	a	35	f	0.4	3	h	5	m	0.13	5	v	0.7	z	1.3	10
Example 4	Manufacturing Example 1	50	Manufacturing Example 5	50	a	35	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	8
Example 5	Manufacturing Example 1	50	Manufacturing Example 5	50	a	25	f	0.8	3	h	10	l	0.36	2.5	v	1.2	y	1.3	10
Example 6	Manufacturing Example 1	30	Manufacturing Example 6	70	a	30	f	0.8	3	h	5	m	0.13	2.5	v	0.7	aa	1.3	9
Example 7	Manufacturing Example 2	70	Manufacturing Example 5	30	a	30	f	0.8	3	h	10	l	0.36	2.5	v	1.2	y	1.3	10
Example 8	Manufacturing Example 1	50	Manufacturing Example 4	50	b	30	f	0.8	3	h	5	k	0.26	7.5	v	0.7	aa	1.3	8
Example 9	Manufacturing Example 1	50	Manufacturing Example 4	50	c	25	f	0.8	3	h	5	k	0.26	7.5	v	0.7	y	1.3	7
Example 10	Manufacturing Example 3	50	Manufacturing Example 4	50	a	35	g	0.4	3	h	10	l	0.36	2.5	v	1.2	aa	1.3	8
Example 11	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.4	1.5	h	5	r	0.01	7.5	v	0.7	y	1.3	7
Example 12	Manufacturing Example 1	50	Manufacturing Example 5	50	a	35	f	0.4	1.5	h	10	s	1.00	2.5	v	1.2	y	1.3	8
Example 13	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.4	1.5	h	5	k	0.26	0.01	v	0.7	y	1.3	7
Example 14	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.4	1.5	h	10	l	0.36	10	v	1.2	y	1.3	9
Example 15	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.8	3	i	10	l	0.36	7.5	v	0.7	y	1.3	7
Example 16	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.8	3	j	10	l	0.36	7.5	v	0.7	y	1.3	7
Example 17	Manufacturing Example 1	20	Manufacturing Example 5	80	a	35	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	9
Example 18	Manufacturing Example 1	90	Manufacturing Example 5	10	a	35	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	9
Comparative Example 1	Manufacturing Example 1	50	Manufacturing Example 5	50	a	35	f	0.4	1.5	h	5	z	z	z	v	0.7	x	1.3	9
Comparative Example 2	Manufacturing Example 1	50	Manufacturing Example 5	50	a	35	f	0.4	-	h	5	k	0.26	<u>30</u>	v	0.7	x	1.3	7
Comparative Example 3	Manufacturing Example 1	50	Manufacturing Example 5	50	a	25	f	0.8	-	h	10	k	0.26	<u>30</u>	v	1.2	y	1.3	10
Comparative Example 4	Manufacturing Example 1	70	Manufacturing Example 5	30	a	30	f	0.8	4.5	h	5	n	<u>1.91</u>	2.5	v	1.2	y	1.3	7
Comparative Example 5	Manufacturing Example 3	70	Manufacturing Example 5	30	a	35	f	0.4	3	h	5	o	<u>1.66</u>	2.5	v	0.7	z	1.3	7
Comparative Example 6	z	z	Manufacturing Example 5	100	a	25	f	0.8	3	h	10	k	0.26	2.5	v	1.2	y	1.3	15
Comparative Example 7	Manufacturing Example 3	50	Manufacturing Example 7	50	a	30	f	0.8	3	h	5	k	0.26	2.5	v	1.2	w	1.3	11
Comparative Example 8	Manufacturing Example 3	50	Manufacturing Example 9	50	a	30	f	0.8	3	h	5	k	0.26	2.5	v	1.2	w	1.3	11
Comparative Example 9	Manufacturing Example 3	50	Manufacturing Example 4	50	a	30	f	0.8	3	h	5	<u>p</u>	0.25	2.5	v	1.2	x	1.3	10
Comparative Example 10	Manufacturing Example 3	50	Manufacturing Example 4	50	a	30	f	0.8	3	h	5	<u>q</u>	0.17	2.5	v	1.2	aa	1.3	9
Comparative Example 11	Manufacturing Example 1	100	z	z	a	30	f	0.8	-	h	5	k	0.26	2.5	v	1.2	x	1.3	7
Comparative Example 12	Manufacturing Example 1	30	Manufacturing Example 8	70	a	25	f	0.8	3	h	10	k	0.26	2.5	v	1.2	x	1.3	14
Comparative Example 13	Manufacturing Example 1	50	Manufacturing Example 5	50	<u>d</u>	35	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	10
Comparative Example 14	Manufacturing Example 1	50	Manufacturing Example 5	50	<u>e</u>	35	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	10
Comparative Example 15	Manufacturing Example 1	50	Manufacturing Example 5	50	z	z	f	0.4	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	8
Comparative Example 16	Manufacturing Example 1	50	Manufacturing Example 5	50	a	30	z	z	1.5	h	5	l	0.36	7.5	v	0.7	y	1.3	8
Comparative Example 17	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.4	7.5	h	5	t	<u>0.003</u>	2.5	v	0.7	x	1.3	7
Comparative Example 18	Manufacturing Example 1	50	Manufacturing Example 4	50	a	25	f	0.8	7.5	h	10	u	<u>2.82</u>	2.5	v	1.2	y	1.3	10
Comparative Example 19	Manufacturing Example 1	50	Manufacturing Example 4	50	a	35	f	0.4	7.5	h	5	k	0.26	<u>0.001</u>	v	0.7	x	1.3	8
Comparative Example 20	Manufacturing Example 1	50	Manufacturing Example 4	50	a	25	f	0.8	7.5	h	10	l	0.36	<u>15</u>	v	1.2	y	1.3	10
Comparative Example 21	Manufacturing Example 1	30	Manufacturing Example 8	70	a	25	f	0.8	3	h	10	k	0.26	2.5	v	1.2	x	1.3	145

Underlined parts indicate outside of the range of the present invention.

[0119]

<Production of Coated Steel Sheet for Evaluation>

Using the aqueous coating agents for a steel material of Examples 1 to 18 and Comparative Examples 1 to 21, a coating film was formed on surfaces of hot-dip galvanized steel sheets and aluminum-containing galvanized steel materials to produce samples for evaluation. The aqueous coating agent for a steel material was applied using a bar coater so that an amount of a dry coating film was 1 g/m², and baked to an achieving sheet temperature of 150°C using a hot air drying furnace having an atmospheric temperature of 500°C to produce a test sheet.

[0120]

<Evaluation>

Using the test sheets according to the examples and the comparative examples produced above, alkali resistance, solvent resistance, abrasion resistance, flat surface corrosion resistance, weather resistance (chroma change amount), glossiness, chroma, and coatability were evaluated under the following conditions. The results are shown in Table 7.

[0121]

(Alkali Resistance)

The test sheet was immersed in a 2 mass% aqueous solution (pH 12.5) of an alkaline degreasing agent (SURFCLEANER 53, manufactured by Nippon Paint Surf Chemicals Co., Ltd.) at 55°C for 2 minutes while being stirred, edges and rear surfaces of the test sheet were then sealed with a tape, and a salt spray testing (JIS-Z-2371) was performed. A state in which white rust had been generated after 72 hours was observed and evaluated according to the following criteria, and 3 was evaluated as acceptable. The results are shown in Table 7.

3: Almost no white rust

2: White rust area less than 30%

1: White rust area 30% or more

[0122]

(Solvent Resistance)

The test sheet was placed on a rubbing tester, and then rubbed with cotton wool impregnated with ethanol, methyl ethyl ketone (MEK), or white gasoline with a load of 0.5 kgf/cm² five times (reciprocating). Thereafter, the edges and rear surfaces of the test sheet were sealed with a tape, and a salt spray test (JIS-Z-2371) was performed. A state in which white rust had been generated after 72 hours was observed and evaluated according to the following criteria, and 3 was evaluated as acceptable. The results are shown in Table 7.

3: Almost no white rust

2: White rust area less than 30%

1: White rust area 30% or more

[0123]

(Ablation Resistance [Sliding Ability])

A load of 10 g/cm² was applied to the test sheet via a corrugated sheet, and an elliptical motion of 360 times/min was applied to cause abrasion (wear scratches) on a sliding portion. After conducting the test for 10 minutes, a surface state of the test sheet was observed and evaluated according to the following criteria, and 3 was evaluated as acceptable. The results are shown in Table 7.

3: Almost no blackening

2: Less than 50% of the area of the sliding portion was blackened

1: 50% or more of the area of the sliding portion was blackened

[0124]

(Flat Portion Corrosion Resistance)

The edges and rear surfaces of the test sheet were sealed with a tape, and the test sheet was subjected to a salt spray test SST (JIS-Z-2371). A state in which white rust had been generated was observed after 72 hours for the hot-dip galvanized test piece and after 120 hours for the aluminum-containing galvanized test piece and evaluated according to the following criteria, and 3 was evaluated as acceptable. The results are shown in Table 7.

3: Almost no white rust

2: White rust area less than 30%

1: White rust area 30% or more

[0125]

(Weather Resistance [Amount of Change in Chroma])

The test sheet was placed in a sunshine weather meter tester and subjected to an accelerated weathering test for 500 hours, and an initial value and an amount of change in chroma after the test were measured. The chroma was calculated as a chroma C^* by the same method as a chroma measurement described below. The amount of change in chroma C^* was calculated by Expression (2), and evaluated according to the following criteria, and 3 was evaluated as acceptable. As the tester, Sunshine Weather Meter manufactured by Suga Test Instruments Co., Ltd. was used. The results are shown in Table 7.

Amount of change (%) = chroma C^* after test / initial value chroma C^* $\times$ 100
... (2)

3: Amount of change (%) = 95% to 100%

2: Amount of change (%) = 90% to less than 95%

1: Amount of change (%) = 80% to less than 90%

[0126]

(Glossiness [Designability])

Using a gloss meter (VG2000 manufactured by NIPPON DENSHOKU INDUSTRIES Co., LTD), a 60° glossiness (%) of the surface of the test sheet was measured based on the method specified in JIS Z 8741. Evaluation was performed according to the following criteria, and 2 was evaluated as acceptable. The results are shown in Table 7.

2: 50% to 200%

1: Less than 50%

[0127]

(Chroma [Designability])

L* a* b* values of the surface of the test sheet were measured using a spectrophotometer (SE6000 manufactured by NIPPON DENSHOKU INDUSTRIES Co., LTD.), and the chroma C* was calculated by the following expression. Evaluation was performed according to the following criteria, and 3 was evaluated as acceptable. The results are shown in Table 7.

3: C* = 2.0 to 50

2: C* = more than 50 and less than 100

1: C* = less than 2.0

[0128]

[Expression 2]

$$\text{Chroma : } (C^*) = \sqrt{(a^*)^2 + (b^*)^2}$$

[0129]

(Coatability)

The aqueous coating agent for a steel material was applied using an automatic bar coater (No. 542-AB manufactured by YASUDA SEIKI SEISAKUSHO, LTD.), and unevenness of the coated external appearance was evaluated according to the following criteria, and 2 was evaluated as acceptable. The results are shown in Table 7.

2: No unevenness

1: There is unevenness

[0130]

[Table 7]

	Hot-dip galvanized steel sheet								Aluminum-containing galvanized steel sheet							
	Alkali resistance	Solvent resistance	Sliding ability	Flat portion corrosion resistance	Chroma C*	Weather resistance	Glossiness	Coatability	Alkali resistance	Solvent resistance	Sliding ability	Flat portion corrosion resistance	Chroma C*	Weather resistance	Glossiness	Coatability
Example 1	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 2	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 3	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 4	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 5	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 6	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 7	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 8	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 9	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 10	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 11	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 12	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 13	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 14	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 15	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 16	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 17	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Example 18	3	3	3	3	3	3	2	2	3	3	3	3	3	3	2	2
Comparative Example 1	3	3	3	3	1	3	2	2	3	3	3	3	1	3	2	2
Comparative Example 2	3	3	3	3	3	3	1	2	3	3	3	3	3	3	1	2
Comparative Example 3	3	3	3	3	3	3	1	2	3	3	3	3	3	3	1	2
Comparative Example 4	3	3	3	2	3	3	1	2	3	3	3	2	3	3	1	2
Comparative Example 5	3	3	3	2	3	3	1	2	3	3	3	2	3	3	1	2
Comparative Example 6	3	3	3	2	3	3	1	2	3	3	3	2	3	3	1	2
Comparative Example 7	3	3	3	2	3	1	2	2	3	3	3	2	3	1	2	2
Comparative Example 8	3	3	3	3	1	1	1	2	3	3	3	3	1	1	1	2
Comparative Example 9	3	3	3	2	3	1	2	2	3	3	3	2	3	1	2	2
Comparative Example 10	3	3	3	2	3	1	2	2	3	3	3	2	3	1	2	2
Comparative Example 11	2	2	2	2	3	1	2	2	2	2	2	2	3	1	2	2
Comparative Example 12	3	3	2	2	3	2	2	2	3	3	2	2	3	2	2	2
Comparative Example 13	3	2	2	2	3	3	2	2	3	2	2	2	3	3	2	2
Comparative Example 14	3	3	3	2	3	3	2	2	3	3	3	2	3	3	2	2
Comparative Example 15	3	2	2	1	3	3	2	2	3	2	2	2	3	3	2	2
Comparative Example 16	2	2	2	1	3	3	2	2	2	2	2	1	3	3	2	2
Comparative Example 17	3	3	3	3	2	3	1	2	3	3	3	3	2	3	1	2
Comparative Example 18	3	3	3	3	2	3	1	2	3	3	3	3	2	3	1	2
Comparative Example 19	3	3	3	2	1	3	2	2	3	3	3	1	3	3	2	2
Comparative Example 20	3	3	3	2	3	3	1	2	3	3	3	2	3	3	1	2
Comparative Example 21	2	2	2	2	2	2	2	1	2	2	2	2	2	2	2	1

[0131]

From the results of Table 7 above, it was confirmed that the steel sheets with a coating film formed of the aqueous coating agent for a steel material of Examples 1 to 18 were excellent in both glossiness and chroma compared to the steel sheets with a coating film formed of the aqueous coating agent for a steel material of Comparative Examples 1 to 21, so that excellent designability was achieved. In addition, the results show that the steel sheets with a coating film formed of the aqueous coating agent for a steel material of Examples 1 to 18 were excellent in alkali resistance, solvent resistance, sliding ability, flat portion corrosion resistance, weather resistance, and coatability.

CLAIMS

What is claimed is:

1. An aqueous coating agent for a steel material comprising:
polyurethane resin particles (A-1) and ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) both having a median diameter of 20 to 100 nm and having a silanol group or an alkoxysilyl group or combination thereof;
silicon oxide particles (B) having a mode size of 5 to 20 nm;
an organic titanium compound (C); and
a phthalocyanine pigment (F) coated with a resin or a surfactant or combination thereof,

wherein an amount of the phthalocyanine pigment (F) is 0.01 to 10 parts by mass with respect to a total of 100 parts by mass of the polyurethane resin particles (A-1) and the ethylene-unsaturated carboxylic acid copolymer resin particles (A-2), and a primary particle size of the phthalocyanine pigment (F) is 0.01 to 1.0 μm .
2. The aqueous coating agent for a steel material according to claim 1,
wherein a phthalocyanine in the phthalocyanine pigment (F) is a metal phthalocyanine or a metal-free phthalocyanine or combination thereof, and
a metal of the metal phthalocyanine is any one of Ca, Ba, Cd, Na, Cu, Ni, Co, Fe, Mg, Zn, Al, Mn, V, Ti, and Sn.
3. The aqueous coating agent for a steel material according to claim 1 or 2,
wherein a 20°C viscosity of the aqueous coating agent for a steel material is 100 mPa·s or less.
4. The aqueous coating agent for a steel material according to any one of claims 1 to 3,
wherein a mass ratio between the polyurethane resin particles (A-1) and the

ethylene-unsaturated carboxylic acid copolymer resin particles (A-2) is (A-1):(A-2) = 20:80 to 90:10.

5. The aqueous coating agent for a steel material according to any one of claims 1 to 4, further comprising:

silicon oxide particles (E) having a mode size of 70 to 200 nm.

6. A coating film formed of the aqueous coating agent for a steel material according to any one of claims 1 to 5 and having a chroma C^* of 2.0 or more and 50 or less.

7. A method of coating a steel material, comprising:

applying the aqueous coating agent for a steel material according to any one of claims 1 to 5 onto a surface of a steel material to form a coating film.

8. A steel material having a surface on which a coating film is formed of the aqueous coating agent for a steel material according to any one of claims 1 to 5, and having a 60° glossiness of 50% or more.

9. The steel material according to claim 8,

wherein the steel material is any one of a hot-dip galvanized steel and an aluminum-containing galvanized steel.