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DESCRIPTION

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AQUEOUS SURFACE TREATMENT AGENT FOR
PLATED METAL SHEET, SURFACE TREATED METAL SHEET AND
PROCESS FOR PRODUCTION THEREOF

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Technical Field

The present invention relates to a surface treated metal sheet with excellent corrosion resistance of flat test piece, corrosion resistance after Erichsen drawing, solvent resistance, coating adhesion and weldability, as well as excellent scratch resistance, and to an aqueous surface treatment agent and production process by which the sheet can be obtained.

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Background Art

Zinc and zinc-based plated steel sheets are conventionally and widely used for household electrical appliances, construction materials and the like. Such steel sheets by themselves have insufficient corrosion resistance and top coatability, and are therefore subjected to chromate treatment or phosphate treatment. It is common to follow this by forming such as press working or bending, or coating, but such sheets are often used without coating depending on the purpose of use. When used without coating, it has been common to employ surface-treated steel sheets known as chromate treated steel sheets, but these have been associated with problems such as fingerprint adhesion and scratching during the forming or assembly. In order to overcome these problems, chromate treatment of zinc-based plated steel sheet surfaces has been followed by formation of organic resin layers having thicknesses of about 1 μm , to prepare organic composite steel sheets.

Such organic composite steel sheets require film performance including not only fingerprint resistance but also corrosion resistance, solvent resistance, top

coatability and the like. In recent years there has been a demand for an even higher level of surface appearance quality, with emphasis on scratch resistance in particular. This is because of increasing movement in the electrical appliance industry toward direct use without coating after pressing, or recently, pressing without oil or with quick-drying oil, in consideration of step reduction and cost reduction. Steel surfaces are highly susceptible to scratching when sliding against dies under such pressing conditions, while scratches are also produced on the surfaces of the forming articles when the formed articles rub against each other or against the containers housing them (cardboard boxes and the like) when the products are transported after forming. The scratched areas have poor corrosion resistance compared to common coated steel sheet surfaces, and the conspicuous nature of the scratches on the outer appearance inevitably lowers the product quality.

For this reason, several techniques have been proposed relating to surface-treated steel sheets in consideration of top coatability and scratch resistance. Such techniques include the processes described in Japanese Unexamined Patent Publication (Kokai) No. 3-17189 (JP-A-3-17189), Japanese Examined Patent Publication (Kokoku) No. 6-104799 (JP-B-6-104799) and Japanese Unexamined Patent Publication (Kokai) No. 6-292859 (JP-A-6-292859).

Japanese Unexamined Patent Publication (Kokai) No. 3-17189 (JP-A-3-17189) discloses a process relating to a resin film obtained by adding fluorine-based resin particles and silica particles to a urethane-modified polyolefin resin. This process is characterized in that fluorine-based resin particles are used to protect the scratch sections, but the use of a surfactant is absolutely indispensable in order to evenly disperse the fluorine-based resin particles in an aqueous solution,

and using the surfactant results in an overall lower level of corrosion resistance, such that a satisfactory degree of corrosion resistance has not been obtainable.

Japanese Examined Patent Publication (Kokoku) No. 6-104799 (JP-B-6-104799) discloses a process relating to a film containing a polyester-based resin, a crosslinking agent and a polyethylene-based wax with an average molecular weight of 2000-8000. According to this process a polyester resin is used as the base resin, and therefore the hydrolysis resistance of the film itself is insufficient, and it has not been possible to obtain satisfactory corrosion resistance.

Japanese Unexamined Patent Publication (Kokai) No. 6-292859 (JP-A-6-292859) discloses a process relating to a film containing spherical polyethylene wax particles and linear colloidal silica added to a resin containing an ordinary-temperature crosslinking epoxy resin combined with a urethane resin with active hydrogen in the molecule. Colloidal silica has a property whereby it increases the frictional coefficient when it adheres to a solid surface, and when chain-like colloidal silica is used according to this process, the scratch resistance is reduced by the structural properties of the colloidal silica itself. As a result, although this process involves adding spherical polyethylene wax, the drying temperature is at a temperature lower than 100°C, and therefore the polyethylene wax becomes embedded in the resin film, resulting in an insufficient lubricating property and unsatisfactory scratch resistance.

Disclosure of the Invention

The present invention, which has been accomplished with the aim of solving the aforementioned problems associated with the prior art, provides a surface treated metal sheet with excellent corrosion resistance of flat test piece, solvent resistance, coating adhesion and weldability, as well as excellent corrosion resistance

after Erichsen drawing and scratch resistance, and an aqueous surface treatment agent and production process by which the sheet can be obtained.

5 As a result of much diligent research on means of overcoming the problems described above, the present inventors have completed the present invention upon achieving the new discovery that it is effective to use an aqueous surface treatment agent containing an acrylic-based resin polymerized from a specific monomer, and
10 silica.

In other words, the gist of the present invention is as follows.

(1) An aqueous surface treatment agent characterized by comprising an acrylic-based resin, water and 5-35 wt% of colloidal silica in terms of solid weight, wherein the
15 acrylic-based resin is a polymer obtained by polymerization reaction of, in terms of solid weight, (a) 15-76 wt% of a (meth)acrylate unsaturated monomer represented by the following general formula (1):

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25 where R^1 is hydrogen or methyl and R^2 is a linear or branched alkyl of 1-8 carbons, (b) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a carboxyl group in the molecule, (c) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a hydroxyl group in the
30 molecule, (d) 10-30 wt% of styrene, (e) 10-30 wt% of acrylonitrile and (f) 0-10 wt% of an unsaturated monomer which is polymerizable with these monomers, and wherein the acrylic-based resin has a glass transition temperature of 0-30°C.

35 (2) An aqueous surface treatment agent according to (1) above, characterized in that (f) in the acrylic-based resin includes an unsaturated monomer having at least one

functional group selected from among glycidyl, aziridinyl, methylol and silanol in the molecule.

5 (3) An aqueous surface treatment agent according to (1) or (2) above, characterized in that the aqueous surface treatment agent contains a polyolefin wax dispersion at no more than 35 wt% in terms of solid weight.

10 (4) A surface-treated metal material characterized in that it has 0.3-5.0 g/m² of an organic/inorganic composite film comprising an acrylic-based resin and 5-35 wt% of colloidal silica in terms of solid weight on a plated metal sheet, the acrylic-based resin being a polymer obtained by polymerization reaction of, in terms of solid weight, (a) 15-76 wt% of a (meth)acrylate
15 unsaturated monomer represented by the aforementioned general formula (1), (b) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a carboxyl group in the molecule, (c) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a hydroxyl group in the molecule, (d) 10-30
20 wt% of styrene, (e) 10-30 wt% of acrylonitrile and (f) 0-10 wt% of an unsaturated monomer which is polymerizable with these monomers, and the acrylic-based resin having a glass transition temperature of 0-30°C.

25 (5) A surface-treated metal material according to (4) above, characterized in that (f) in the acrylic-based resin includes an unsaturated monomer having at least one functional group selected from among glycidyl, aziridinyl, methylol and silanol in the molecule.

30 (6) A surface-treated metal material according to (4) or (5) above, characterized in that the aqueous surface treatment agent contains a polyolefin wax dispersion at no more than 35 wt% in terms of solid weight.

35 (7) A process for production of a surface-treated metal material, characterized by coating an aqueous surface treatment agent according to any one of (1) to

(3) above onto a plated metal sheet or a surface-prepared plated metal sheet at 0.3-5.0 g/m² in terms of dry solid weight, and then drying it to form an organic/inorganic composite film.

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Best Mode for Carrying Out the Invention

The first aspect of the invention is that the acrylic resin used as the base resin is a copolymer obtained by copolymerization of several different
10 monomers having ethylenic double bonds, the copolymer being obtained by polymerization of suitable amounts of suitable types of monomers. The polymerization method for the polymer used for the invention is not particularly restricted, but methods of suspension
15 polymerization and emulsion polymerization are preferred.

As examples of such monomers there may be mentioned, acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, itaconic acid, citraconic acid, cinnamic acid, 2-hydroxyethyl
20 (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)allylether, 3-hydroxypropyl (meth)allylether, 4-hydroxybutyl (meth)allylether, allyl alcohol, glycidyl
25 (meth)acrylate, 2-(1-aziridinyl)ethyl acrylate, vinyltrimethoxysilane, vinyltriethoxysilane, allylglycidyl ether, iminolmethacrylate, acryloylmorpholine, N-methylol (meth)acrylamide, N-methoxymethyl (meth)acrylamide, N-ethoxymethyl
30 (meth)acrylamide, N-butoxymethyl (meth)acrylamide, (meth)acrylamide, N-methyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, N-dimethylaminopropyl (meth)acrylamide, vinyl formate, vinyl acetate, vinyl butyrate, vinyl
35 acrylate, styrene, α -methylstyrene, t-butylstyrene, vinyltoluene, (meth)acrylonitrile, cinnamyl nitrile, (meth)acryloxyethyl phosphate, bis-(meth)acryloxyethyl

phosphate, (meth)acryloxyethylphenyl acid phosphate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate and its isomers, butyl (meth)acrylate and its isomers, pentyl (meth)acrylate and its isomers and hexyl (meth)acrylate and its isomers. The references to "(meth)acryl", "(meth)acrylate", "(meth)allyl" and "(meth)acryloxy" here signify "acryl" or "methacryl", "acrylate" or "methacrylate", "allyl" or "methallyl" and "acryloxy" or "methacryloxy", respectively, and any other similar references have the same meaning.

It is necessary to use, as the acrylic-based resin, a polymer obtained by polymerization reaction of, in terms of solid weight, (a) 15-76 wt% of a (meth)acrylate unsaturated monomer represented by the following general formula (1):



where R^1 is hydrogen or methyl and R^2 is a linear or branched alkyl of 1-8 carbons, (b) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a carboxyl group in the molecule, (c) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a hydroxyl group in the molecule, (d) 10-30 wt% of styrene, (e) 10-30 wt% of acrylonitrile and (f) 0-10 wt% of an unsaturated monomer which is polymerizable with these monomers.

The (meth)acrylate unsaturated monomer (a) used for the invention is represented by general formula (1) above. As examples there may be mentioned methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate and its isomers, n-butyl (meth)acrylate and its isomers, n-pentyl (meth)acrylate and its isomers, n-hexyl (meth)acrylate and its isomers, n-heptyl (meth)acrylate and its isomers and n-octyl (meth)acrylate and its isomers.

The content of the unsaturated monomer (a) is 15-76 wt% and preferably 30-70 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f) composing the acrylic-based resin. If the content of the unsaturated monomer (a) is less than 15 wt%, the resulting polymer film lacks flexibility, cracks tend to occur in the film during film formation, and sufficient corrosion resistance cannot be obtained. On the other hand, the content is preferably not greater than 76 wt% because the solvent resistance of the formed film is inferior.

As examples of the α,β -ethylenic unsaturated monomer (b) with a carboxyl group in the molecule, to be used for the invention, there may be mentioned acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, crotonic acid, itaconic acid, citraconic acid and cinnamic acid. The content of the unsaturated monomer (b) is preferably 2-10 wt% and more preferably 2.5-8 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f) composing the acrylic-based resin. At less than 2 wt% the adhesion of the film for steel sheets is inferior, and at greater than 10 wt% the corrosion resistance and water resistance of the film is inferior.

As examples of the α,β -ethylenic unsaturated monomer (c) with a hydroxyl group in the molecule, to be used for the invention, there may be mentioned 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 3-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, 2-hydroxyethyl (meth)allylether, 3-hydroxypropyl (meth)allylether, 4-hydroxybutyl (meth)allylether and allyl alcohol. The content of the unsaturated monomer (c) is preferably 2-10 wt% and more preferably 2.5-8 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f)

composing the acrylic-based resin. At less than 2 wt% the adhesion of the film for steel sheets is inferior, and at greater than 10 wt% the corrosion resistance and water resistance of the film is inferior.

5 The content of the styrene (d) used for the invention is preferably 10-30 wt% and more preferably 12-25 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f) composing the acrylic-based resin. At less than 10 wt% the scratch resistance
10 of the formed film is inferior, and at greater than 30 wt% the corrosion resistance after Erichsen drawing of the film is inferior.

 The content of the acrylonitrile (e) used for the invention is preferably 10-30 wt% and more preferably 15-
15 28 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f) composing the acrylic-based resin. At less than 10 wt% the solvent resistance of the formed film is inferior, and at greater than 30 wt% the water resistance and corrosion resistance of the
20 film is inferior.

 The unsaturated monomer (f) is an unsaturated monomer other than (a) to (e), which is copolymerizable with monomers (a) to (e), and any one may be used for the purpose of further enhancing the solvent resistance,
25 adhesion, scratch resistance, etc. of the formed film, so long as the effect of the invention is not hindered.

 As examples of the unsaturated monomer (f) there may be mentioned amide group-containing unsaturated monomers such as (meth)acrylamide, N-methyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide and N-dimethylaminopropyl
30 (meth)acrylamide; esterified unsaturated monomers such as vinyl formate, vinyl acetate, vinyl butyrate and vinyl acrylate; aromatic unsaturated monomers such as styrene, α -methylstyrene, t-butylstyrene and vinyltoluene;
35 cyanated unsaturated monomers such as (meth)acrylonitrile and cinnamyl nitrile; phosphate group-containing unsaturated monomers such as (meth)acryloxyethyl

phosphate, bis-(meth)acryloxyethyl phosphate and (meth)acryloxyethylphenyl acid phosphate; and unsaturated monomers with functional groups that can react with hydroxyl and carboxyl groups, such as glycidyl (meth)acrylate, 2-(1-aziridinyl)ethyl acrylate, vinyltrimethoxysilane, vinyltriethoxysilane, allylglycidyl ether, iminol methacrylate, acryloylmorpholine, N-methylol (meth)acrylamide, N-methoxymethyl (meth)acrylamide, N-ethoxymethyl (meth)acrylamide and N-butoxymethyl (meth)acrylamide. Preferably, at least one among these is an unsaturated monomer with a functional group that can react with hydroxyl or carboxyl group, and more preferably, an unsaturated monomer containing a glycidyl, aziridinyl, methylol or silanol group. As examples of such compounds there may be mentioned glycidyl (meth)acrylate, 2-(1-aziridinyl)ethyl acrylate, vinyltrimethoxysilane, vinyltriethoxysilane, allylglycidyl ether, iminol methacrylate, acryloylmorpholine, N-methylol (meth)acrylamide, N-methoxymethyl (meth)acrylamide, N-ethoxymethyl (meth)acrylamide and N-butoxymethyl (meth)acrylamide. The content of the unsaturated monomer (f) preferably does not exceed 10 wt% with respect to 100 wt% of the total of the unsaturated monomers (a) to (f) composing the acrylic-based resin, because the polymer tends to increase in viscosity, the working life of the aqueous surface treatment agent is shortened, a uniform film cannot be formed, and the corrosion resistance is impaired.

30 The glass transition temperature of the acrylic-based resin used for the invention is preferably 0-30°C. The glass transition temperature of the acrylic-based resin is preferably not below 0°C because the blocking resistance of the formed film is inferior. It is also preferably not above 30°C because the film forming property is reduced and the corrosion resistance after Erichsen drawing is inferior.

The glass transition temperature (T_g) in the invention is the value calculated based on the T_g of the homopolymer of each monomer component, and it may be determined by the following formula.

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$$1/T_g = W_1/T_{g1} + W_2/T_{g2} + \dots + W_n/T_{gn}$$

Here, T_g is the glass transition temperature of the polymer, T_{g1}, T_{g2},...T_{gn} are the respective glass transition temperatures of homopolymers of the monomer components and w₁, w₂...w_n represent the weight fractions of each monomer, where w₁ + w₂ + ... w_n = 1. The glass transition temperatures of the homopolymers of each monomer are determined according to JIS K 7121.

15 The content of the colloidal silica in the aqueous surface treatment agent of the invention and the film of the surface treated metal material is 5-35 wt% in terms of solid weight. The content of colloidal silica is preferably not less than 5 wt% because the corrosion resistance of the film is inferior. It is also preferably not greater than 35 wt% because the binder effect of the resin is reduced, and the corrosion resistance is lowered. The particle diameter and type of the colloidal silica are not particularly restricted according to the invention, and for example, the commercially available products SNOWTEX O, C and N by Nissan Chemical Industries, Ltd. and ADELITE AT-20N, A and Q by Asahi Denka Kogyo K.K. may be used.

25 For enhancement of the scratch resistance of the surface-treated metal material according to the invention, a polyolefin wax dispersion may also be added to the aqueous surface treatment agent and organic/inorganic composite film.

30 As polyolefin wax dispersions there may be used dispersions of polyethylene wax, polypropylene wax or polybutylene wax, or their modified polyolefin waxes obtained by addition of polar groups to these waxes, in

water or aqueous solutions with an emulsifier concentration of no greater than 5% and preferably with no emulsifier. The polar groups may be introduced by oxidizing treatment of the polyolefin wax with an oxidizing agent such as oxygen, ozone or nitric acid, in the presence of a catalyst (to obtain an oxidized polyolefin wax), or they may be introduced by dissolving an ethylenic unsaturated carboxylic acid monomer such as acrylic acid, methacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid in benzole or the like together with the polyolefin wax, and heating the solution in a nitrogen stream together with a polymerization initiator (peroxide, redox, heavy metal catalyst, etc.), for grafting.

The weight-average particle size of the polyolefin wax dispersion is preferably 0.1-5.0 μm , and more preferably 1.0-4.0 μm . The weight-average particle size is preferably not less than 0.1 μm because the particles tend to aggregate, thus impairing the stability. The weight-average particle size is also preferably not greater than 5.0 μm because the particle dispersion stability is impaired. The ratio of the weight-average particle size and the number-average particle size is preferably in a range such that (weight-average particle size/number-average particle size) < 3.

The polyolefin wax dispersion is preferably included in the aqueous surface treatment agent and organic/inorganic composite film at no greater than 35 wt% in terms of solid weight. This is because at greater than 35 wt%, the coating adhesion is inferior.

According to the invention, the organic/inorganic composite film is formed on a metal sheet at a coverage of 0.3-5.0 g/m^2 in terms of solid weight. At less than 0.3 g/m^2 , the scratch resistance of the film is inferior, and its corrosion resistance after Erichsen drawing is unsatisfactory. On the other hand, at greater than 5.0

g/m² the weldability is inferior.

The aqueous surface treatment agent used for the invention may also contain a surfactant known as a wetting enhancer to obtain a uniform film on the coating surface, thickening agent, a conductive substance for enhanced weldability, a coloring pigment and a delustering agent for enhanced decoration, a solvent for improved film formability, and the like, so long as the effect of the invention is not hindered.

Plated metal sheet substrate which may be used for the invention include zinc-based electroplated, hot-dip plated and evaporation plated steel sheets, such as zinc-plated metal sheets, zinc-nickel plated metal sheets, zinc-iron plated metal sheets, zinc-chromium plated metal sheets, zinc-aluminum plated metal sheets, zinc-titanium plated metal sheets, zinc-magnesium plated metal sheets and zinc-manganese plated metal sheets, and aluminum- or aluminum alloy-plated metal sheets, lead- or lead alloy-plated metal sheets, tin- or tin alloy-plated metal sheets, as well as those having such a plated layer containing small amounts of cobalt, molybdenum, tungsten, nickel, titanium, chromium, aluminum, manganese, iron, magnesium, lead, antimony, tin, copper, cadmium, arsenic or the like as dissimilar metal elements or impurities, and/or having dispersed therein inorganic substances such as silica, alumina or titania. In addition, other types of platings than those mentioned above, such as iron platings, iron-phosphorus platings and the like, may be combined therewith for composite layer-plated metal sheets.

The aqueous surface treatment agent of the invention may be directly coated onto the plated metal sheet, but in order to achieve a sufficient effect according to the invention, preferably a substrate film is first formed by chromate treatment or non-chromate treatment by an ordinary process, and then the aqueous surface treatment agent of the invention is coated thereover to form a

resin film.

If chromate treatment employed, then according to the invention it may be any treatment such as electrolytic chromate treatment whereby a chromate film is formed by electrolysis, reactive chromate treatment whereby reaction with a stock material is used to form a film and then the excess treatment solution is rinsed off, or application chromate treatment whereby the treatment solution is applied onto the material to be coated and then dried without water washing to form a film.

If non-chromate treatment is employed, then according to the invention it may be any treatment such as electrolytic non-chromate treatment whereby a non-chromate film is formed by electrolysis, reactive non-chromate treatment whereby reaction with a stock material is used to form a film and then the excess treatment solution is rinsed off, or application non-chromate treatment whereby the treatment solution is applied onto the material to be coated and then dried without water washing to form a film.

Applying the aqueous surface treatment agent of the invention onto a plated metal sheet substrate treated by the aforementioned chromate treatment and drying it at a peak metal temperature of 60-200°C forms an organic/inorganic composite film. The application method employed may be a common method such as roll coating, immersion or electrostatic spray coating.

Examples

The present invention will now be explained in greater detail by way of production examples, working examples and comparative examples. The examples are intended to serve as illustration of the invention and are not meant to restrict the invention in any way.

(1) Metal sheets

The metal sheets used are listed in Table 1.

Table 1 Types of metal sheets and plating coverages
(sheet thickness: 0.8 mm)

Abbreviation	Type of metal sheet
EG	Zinc electroplated steel sheet (plating coverage: 20 g/m ²)
ZN	Zinc/nickel electroplated steel sheet (plating coverage: 20 g/m ² , nickel content: 12 wt%)
GI	Zinc hot-dip plated steel sheet (plating coverage: 60 g/m ²)

5 (2) Degreasing treatment

Each metal sheet was subjected to degreasing treatment with the silicate-based alkali degreasing agent Fine Cleaner 4336 (registered trademark of Nihon Parkerizing Co., Ltd.). Specifically, the metal sheet
10 was treated for 2 minutes by spraying with a degreasing agent concentration of 20 g/l at a temperature of 60°C, after which it was spray washed with tap water for 30 seconds.

(3) Substrate layer treatment

15 (a) Reactive chromate treatment (metal sheets: EG, ZN, GI)

Zinc-Chrome 357 (registered trademark of Nihon Parkerizing Co., Ltd.) was used for spray treatment of the metal sheet for 5 seconds at a solution temperature
20 of 50°C, followed by washing with tap water and air drying to fabricate a sample sheet. The target chromium coverage was 20 mg/m².

(b) Application chromate chemical treatment (metal sheets: EG, ZN, GI)

25 Zinc-Chrome 1300AN (registered trademark of Nihon Parkerizing Co., Ltd.) was applied onto the metal sheet by roll coating, and then drying was performed immediately at an atmosphere temperature of 200°C for 10 seconds without water washing to fabricate a sample
30 sheet. The peak metal temperature for the treatment was 100°C, and the target chromium coverage was 40 mg/m².

(c) Electrolytic chromate treatment (metal sheets:

EG, ZN, GI)

A prescribed amount of electricity was applied at a current density of 10 A/dm² in a bath containing 50 g/l of chromic acid and 0.3 g/l of sulfuric acid, for electrolytic chromate treatment of the metal sheet, and after water washing, drying was performed for 8 seconds at an atmosphere temperature of 200°C to fabricate a sample sheet. The peak metal temperature for the treatment was 80°C, and the target chromium coverage was 40 mg/m².

(4) Preparation of aqueous surface treatment agents

The (a) (meth)acrylate unsaturated monomers, (b) α,β -ethylenic unsaturated monomers with a carboxyl group in the molecule, (c) α,β -ethylenic unsaturated monomers with a hydroxyl group in the molecule, (d) styrene, (e) acrylonitrile and (f) unsaturated monomer polymerizable with these monomers, having the abbreviations shown in Table 2, were used in the proportions shown in Table 3 to obtain polymers A1 to A37 shown in Table 3. The value in parentheses following the name of each of the monomers in Table 2 represents the glass transition temperature (T_g) in °C of the homopolymer of that monomer component, and the T_g values at the right of Table 3 are the glass transition temperatures of each of the polymers.

Aqueous dispersions of the polymer of Table 3 and the colloidal silica and polyolefin wax dispersions of Tables 4 and 5, respectively, were mixed at room temperature in the proportions shown in Tables 7 to 12 using a propeller stirrer, and distilled water was added to adjust the solid concentrations. The solid compositions of the films shown in Tables 7 to 12 are based on 100 wt% as the total of the polymer, silica and wax, and the silica and wax amounts in the tables are represented as weight percentages.

Table 2

Monomer	Abbrevia- tion	Name	Abbrevia- tion	Name
(a)	BA	n-butyl acrylate (-54)	2EHA	2-ethylhexyl acrylate (-85)
	BMA	n-butyl methacrylate (20)	MMA	methyl methacrylate (105)
(b)	AA	acrylic acid (106)	MAA	methacrylic acid (130)
(c)	2HEMA	2-hydroxyethyl methacrylate (55)	2HEA	2-hydroxyethyl acrylate (-15)
	HPMA	hydroxypropyl methacrylate (26)		
(d)	St	styrene (100)		
(e)	AN	acrylonitrile (100)		
(f)	GMA	glycidyl methacrylate (41)	N-MAAm	N-methylolacrylamide (75)

5

Table 3

No.	Monomer types and their proportions in polymers															Tg
	(a)					(b)		(c)		(d)		(e)		(f)		
	Type	Wt%	Type	Wt%	Total	Type	Wt%	Type	Wt%	Type	Wt%	Type	Wt%	Type	Wt%	
A1	BA	25	BMA	30	55	AA	5	2HEMA	5	St	10	AN	25	-	-	22
A2	BA	30	BMA	15	45	AA	2.5	2HEMA	2.5	St	25	AN	25	-	-	24
A3	BA	45	-	0	45	MAA	2.5	2HEMA	2.5	St	25	AN	25	-	-	10
A4	BA	49	-	0	49	AA	3	2HEMA	3	St	20	AN	25	-	-	3.7
A5	2EHA	25	BMA	22	47	MAA	3	HEMA	5	St	20	AN	25	-	-	10
A6	2EHA	25	BMA	22	47	MAA	4	2HEA	4	St	20	AN	25	-	-	9.4
A7	BA	45	-	0	45	AA	5	2HEMA	5	St	20	AN	25	-	-	9.0
A8	BA	58	-	0	58	AA	5	2HEMA	5	St	7	AN	25	-	-	-9.2
A9	BA	38	BMA	35	73	AA	5	2HEMA	2	St	10	AN	10.0	-	-	0
A10	BA	20	BMA	31	51	AA	5	2HEMA	5	St	14	AN	25.0	-	-	30
A11	BA	20	BMA	20	40	AA	5	2HEMA	5	St	25	AN	25	-	-	37
A12	BA	45	-	-	45	-	-	2HEMA	5	St	25	AN	25	-	-	8.9
A13	BA	45	-	0	45	AA	2	2HEMA	5	St	23	AN	25	-	-	8.9
A14	BA	45	-	0	45	AA	10	2HEMA	5	St	15	AN	25	-	-	9.2
A15	BA	45	-	-	45	AA	15	2HEMA	5	St	10	AN	25	-	-	9.4
A16	BA	38	BMA	22	60	AA	5	-	-	St	20	AN	15	-	-	8.2
A17	BA	36	BMA	22	58	AA	5	2HEMA	2	St	20	AN	15	-	-	11
A18	BA	28	BMA	22	50	AA	5	2HEMA	10	St	20	AN	15	-	-	21
A19	BA	23	BMA	22	45	AA	5	2HEMA	15	St	20	AN	15	-	-	27
A20	BA	30	BMA	40	70	AA	5	2HEMA	5	-	-	AN	20	-	-	8.2
A21	BA	30	BMA	30	60	AA	5	2HEMA	5	St	10	AN	20	-	-	14
A22	BA	30	BMA	10	40	AA	5	2HEMA	5	St	30	AN	20	-	-	27
A23	BA	30	BMA	5	35	AA	5	2HEMA	5	St	35	AN	20	-	-	30
A24	BA	50	BMA	20	70	AA	5	2HEMA	5	St	20	-	-	-	-	-8.9
A25	BA	40	BMA	20	60	AA	5	2HEMA	5	St	20	AN	10	-	-	5.0
A26	BA	40	-	0	40	AA	5	2HEMA	5	St	20	AN	30	-	-	17
A27	BA	35	-	-	35	AA	5	2HEMA	5	St	20	AN	35	-	-	25
A28	BA	40	BMA	6	46	AA	5	2HEMA	5	St	20	AN	20	NMAAm	4	12
A29	BA	34	BMA	6	40	AA	5	2HEMA	5	St	20	AN	20	NMAAm	10	21
A30	BA	29	BMA	6	35	AA	5	2HEMA	5	St	20	AN	20	NMAAm	15	28
A31	BA	42	BMA	5	47	MAA	2.5	2HEMA	2.5	St	20	AN	25	GMA	3	7.7
A32	BA	35	BMA	5	40	MAA	2.5	2HEMA	2.5	St	20	AN	25	GMA	10	9.1
A33	BA	30	BMA	5	35	MAA	2.5	2HEMA	2.5	St	20	AN	25	GMA	15	10.1
A34	2EHA	10	-	-	10	AA	10	2HEA	10	St	30	AN	30	GMA	10	37
A35	2EHA	15	-	0	15	AA	10	2HEA	10	St	30	AN	25	GMA	10	25
A36	BA	40	MMA	36	76	MAA	2	2HEMA	2	St	10	AN	10	-	-	19
A37	BA	40	MMA	40	80	MAA	2	2HEMA	2	St	10	AN	6	-	-	19

Table 4

No.	Type
B1	ADELITE AT-20N, Asahi Denka Kogyo K.K.
B2	SNOWTEX N, Nissan Chemical Industries Co., Ltd.

5

Table 5

No.	Type
C1	Polyethylene wax dispersion, particle size 3.0 μm
C2	Polyethylene wax dispersion, particle size 1.0 μm
C3	Polyethylene wax dispersion, particle size 0.6 μm

10 (5) Method of application of aqueous surface treatment agents onto sample sheets

The respective aqueous surface treatment agents prepared as described above were applied onto the aforementioned sample sheets using a bar coater, and
15 drying was performed for 12 seconds at an atmosphere temperature of 280°C. The peak metal temperature for this treatment was 130°C, and the target coverage was 1.0 g/m². The coverage was adjusted by appropriately changing the solid concentration of the treatment agent
20 and the type of bar coater.

(6) Surface-treated metal sheet performance test

(a) Corrosion resistance of flat test pieces

Following the salt spray test method described by JIS Z 2371, the surface-treated metal sheet sample was
25 sprayed with a 5% NaCl aqueous solution at an atmosphere temperature of 35°C, and the white rust generation was measured after 72 hours. Samples assigned ◎ or ○ on the following evaluation scale were judged as satisfactory. The results are shown in Tables 7 to 12.

30 <Evaluation scale>

◎: White rust area of <5% of total area

○: White rust area of ≥5% and <10% of total area

△: White rust area of $\geq 10\%$ and $< 30\%$ of total area

X: White rust area of $\geq 30\%$ of total area

(b) Corrosion resistance after Erichsen drawing

The surface-treated metal sheet sample was subjected
5 to 6 mm Erichsen drawing and then, following the salt
spray test method described by JIS Z2371, the surface-
treated metal sheet sample was sprayed with a 5% NaCl
aqueous solution at an atmosphere temperature of 35°C ,
and the white rust generation at the drawn section was
10 measured after 48 hours. Samples assigned ◎ or ○ on the
following evaluation scale were judged as satisfactory.
The results are shown in Tables 7 to 12.

<Evaluation scale>

◎: White rust area of $< 5\%$ of drawn section area

15 ○: White rust area of $\geq 5\%$ and $< 10\%$ of drawn section area

△: White rust area of $\geq 10\%$ and $< 30\%$ of drawn section
area

X: White rust area of $\geq 30\%$ of drawn section area

(c) Solvent resistance

20 The surface of the surface-treated metal sheet
sample was rubbed for 10 full passes, using gauze soaked
with a solvent (ethanol or MEK), under a 500 g weight.
The appearance was observed after the rubbing, and
samples assigned ◎ or ○ on the following evaluation
25 scale were judged as satisfactory. The results are shown
in Tables 7 to 12.

<Evaluation scale>

◎: Film swelling area of $< 30\%$ of total rubbed area

○: Film swelling area of $\geq 30\%$ of total rubbed area

30 △: Film dissolved area of $< 30\%$ of total rubbed area

X: Film dissolved area of $\geq 30\%$ of total rubbed area

(d) Coating adhesion

The surface-treated metal sheet sample was coated
with a melamine alkyd resin paint (Amilack #1000, product
35 of Kansai Paint Co., Ltd.) to a dry film thickness of 25

um using a bar coater, and baked for 20 minutes at a furnace temperature of 130°C. After standing overnight, a sample immersed for 30 minutes in boiling water and one not immersed were both subjected to 7 mm Erichsen drawing, and adhesive tape (CELLOTAPE, product name of Nichiban Co.) was attached to the Erichsen drawn section of the sample. The adhesive tape was rapidly pulled at a 45° slant and the appearance of the Erichsen drawn section was visually observed. Samples assigned ◎ or ○ on the following evaluation scale were judged as satisfactory. The results are shown in Tables 7 to 12.

<Evaluation scale>

- ◎: No peeling
- : Peeling area of <5%
- △: Peeling area of ≥5% and <50%
- ×: Peeling area of ≥50%

(e) Press galling resistance

The surface-treated metal sheet sample was subjected to a test of rectangular drawing. The conditions for the rectangular drawing test were a blank folder force of 6 tons and a sample (0.8 x 220 x 180 mm) formed to 65 x 115 mm and a height of 50 mm, and the sliding surface was visually evaluated after forming. Samples assigned ◎ or ○ on the following evaluation scale were judged as satisfactory. The results are shown in Tables 7 to 12.

- ◎: No defect due to galling
- : Defects and sliding scratches on <50% of sliding section area
- △: Defects and sliding scratches on ≥50% of sliding section area
- ×: Exposure of metal substrate, galling

(f) Weldability

The surface-treated metal sheet sample was subjected to a continuous spot welding test under the conditions shown in Table 6, and the number of welding points which

could be stably formed with a nugget diameter of 3 mm or greater was determined.

Table 6 Welding conditions

Parameter	Conditions
Welding current	8500 A
Electrification time	10 cycles (at 50 Hz)
Electrode diameter	4.5 mm
Electrode force	200 kgf

5

Samples assigned ◎ or ○ on the following evaluation scale were judged as satisfactory. The results are shown in Tables 7 to 12.

◎: Welding points: ≥ 5000

10 ○: Welding points: ≥ 2500 , < 5000

△: Welding points: ≥ 1000 , < 2500

×: Welding points: < 1000

Table 7

Mat- erial No.	Substrate layer treatment			Solid composition of film				Coverage g/m ²	Film performance						Note	
	Treatment method	Type	Coverage mg/m ²	Polymer type	Silica		Wax		Corrosion resistance	Coating adhe- sion	Solvent resistance		Press galling resist- ance	Weld- ing abil- ity		
					Amount	Type	Amount				Type	EtOH				MEK
1	EG	electrolysis	chromate	40	A1	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
2	EG	electrolysis	chromate	40	A2	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
3	EG	electrolysis	chromate	40	A3	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
4	EG	electrolysis	chromate	40	A4	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
5	EG	electrolysis	chromate	40	A5	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
6	EG	electrolysis	chromate	40	A6	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
7	EG	electrolysis	chromate	40	A7	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
8	EG	electrolysis	chromate	40	A8	B1	20	C1	5	1.0	⊙	△	△	⊙	⊙	Comp. Ex.
9	EG	electrolysis	chromate	40	A9	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
10	EG	electrolysis	chromate	40	A10	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
11	EG	electrolysis	chromate	40	A11	B1	20	C1	5	1.0	⊙	△	⊙	⊙	⊙	Comp. Ex.
12	EG	electrolysis	chromate	40	A12	B1	20	C1	5	1.0	⊙	⊙	⊙	△	⊙	Comp. Ex.
13	EG	electrolysis	chromate	40	A13	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
14	EG	electrolysis	chromate	40	A14	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
15	EG	electrolysis	chromate	40	A15	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
16	EG	electrolysis	chromate	40	A16	B1	20	C1	5	1.0	⊙	⊙	⊙	△	⊙	Comp. Ex.
17	EG	electrolysis	chromate	40	A17	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
18	EG	electrolysis	chromate	40	A18	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
19	EG	electrolysis	chromate	40	A19	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
20	EG	electrolysis	chromate	40	A20	B1	20	C1	5	1.0	⊙	⊙	△	△	⊙	Comp. Ex.
21	EG	electrolysis	chromate	40	A21	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
22	EG	electrolysis	chromate	40	A22	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
23	EG	electrolysis	chromate	40	A23	B1	20	C1	5	1.0	⊙	△	⊙	⊙	⊙	Comp. Ex.
24	EG	electrolysis	chromate	40	A24	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
25	EG	electrolysis	chromate	40	A25	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
26	EG	electrolysis	chromate	40	A26	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
27	EG	electrolysis	chromate	40	A27	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
28	EG	electrolysis	chromate	40	A28	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
29	EG	electrolysis	chromate	40	A29	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
30	EG	electrolysis	chromate	40	A30	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
31	EG	electrolysis	chromate	40	A31	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
32	EG	electrolysis	chromate	40	A32	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention
33	EG	electrolysis	chromate	40	A33	B1	20	C1	5	1.0	⊙	△	⊙	⊙	⊙	Comp. Ex.
34	EG	electrolysis	chromate	40	A34	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Comp. Ex.
35	EG	electrolysis	chromate	40	A35	B1	20	C1	5	1.0	⊙	⊙	⊙	⊙	⊙	Invention

Table 8

No.	Mat- erial	Substrate layer treatment		Coverage mg/m ²	Solid composition of film				Coverage g/m ²	Film performance					Note	
		Treatment method	Type		Polymer type	Silica		Wax		Corrosion resistance	Coating adhe- sion	Solvent resistance EtOH MEK	Press galling resist- ance	Weld- resistance abil- ity		
						Type	Amount	Type								Amount
36	EG	electrolysis	chromate	40	A36	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
37	EG	electrolysis	chromate	40	A37	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Comp. Ex.	
38	GI	electrolysis	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
39	GI	reactive	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
40	GI	application	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
41	ZN	electrolysis	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
42	ZN	reactive	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
43	ZN	application	chromate	40	A7	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
44	EG	reactive	chromate	40	A10	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
45	EG	application	chromate	40	A10	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
46	EG	electrolysis	chromate	40	A21	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
47	EG	electrolysis	chromate	40	A21	B2	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
48	EG	electrolysis	chromate	40	A21	B1	0	C1	5	⊙	⊙	⊙	⊙	⊙	Comp. Ex.	
49	EG	electrolysis	chromate	40	A21	B1	10	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
50	EG	electrolysis	chromate	40	A21	B1	25	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
51	EG	electrolysis	chromate	40	A21	B1	30	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
52	EG	electrolysis	chromate	40	A21	B1	35	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
53	EG	electrolysis	chromate	40	A21	B1	40	C1	5	⊙	⊙	⊙	⊙	⊙	Comp. Ex.	
54	EG	electrolysis	chromate	40	A25	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Comp. Ex.	
55	EG	electrolysis	chromate	40	A25	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
56	EG	electrolysis	chromate	40	A25	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
57	EG	electrolysis	chromate	40	A25	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Invention	
58	EG	electrolysis	chromate	40	A25	B1	20	C1	5	⊙	⊙	⊙	⊙	⊙	Comp. Ex.	
59	EG	electrolysis	chromate	40	A31	B1	20	-	-	⊙	⊙	⊙	⊙	⊙	Invention	
60	EG	electrolysis	chromate	40	A31	B1	20	C1	0.1	⊙	⊙	⊙	⊙	⊙	Invention	
61	EG	electrolysis	chromate	40	A31	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
62	EG	electrolysis	chromate	40	A31	B1	20	C1	10	⊙	⊙	⊙	⊙	⊙	Invention	
63	EG	electrolysis	chromate	40	A31	B1	20	C1	35	⊙	⊙	⊙	⊙	⊙	Invention	
64	EG	electrolysis	chromate	40	A31	B1	20	C1	40	⊙	⊙	⊙	⊙	⊙	Invention	
65	EG	electrolysis	chromate	40	A31	B1	20	C2	0.1	⊙	⊙	⊙	⊙	⊙	Invention	
66	EG	electrolysis	chromate	40	A31	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
67	EG	electrolysis	chromate	40	A31	B1	20	C2	10	⊙	⊙	⊙	⊙	⊙	Invention	
68	EG	electrolysis	chromate	40	A31	B1	20	C2	35	⊙	⊙	⊙	⊙	⊙	Invention	
69	EG	electrolysis	chromate	40	A31	B1	20	C2	40	⊙	⊙	⊙	⊙	⊙	Invention	
70	EG	electrolysis	chromate	40	A31	B1	20	C3	0.1	⊙	⊙	⊙	⊙	⊙	Invention	
71	EG	electrolysis	chromate	40	A31	B1	20	C3	1	⊙	⊙	⊙	⊙	⊙	Invention	
72	EG	electrolysis	chromate	40	A31	B1	20	C3	10	⊙	⊙	⊙	⊙	⊙	Invention	
73	EG	electrolysis	chromate	40	A31	B1	20	C3	35	⊙	⊙	⊙	⊙	⊙	Invention	
74	EG	electrolysis	chromate	40	A31	B1	20	C3	40	⊙	⊙	⊙	⊙	⊙	Invention	

Table 9

No.	Mat- erial	Substrate layer treatment		Solid composition of film				Coverage g/m ²	Film performance					Note																									
		Treatment method	Type	Coverage mg/m ²	Polymer type	Silica			Wax		Corrosion resistance	Coating adhe- sion	Solvent resistance EtOH MEK		Press galling resist- ance	Weld- abil- ity																							
						Type	Amount		Type	Amount																													
75	EG	electrolysis	chromate	40	A1	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	Invention																							
76	EG	electrolysis	chromate	40	A2	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																						
77	EG	electrolysis	chromate	40	A3	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																					
78	EG	electrolysis	chromate	40	A4	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																				
79	EG	electrolysis	chromate	40	A5	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																			
80	EG	electrolysis	chromate	40	A6	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																		
81	EG	electrolysis	chromate	40	A7	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																	
82	EG	electrolysis	chromate	40	A9	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention																
83	EG	electrolysis	chromate	40	A10	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention															
84	EG	electrolysis	chromate	40	A13	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention														
85	EG	electrolysis	chromate	40	A14	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention													
86	EG	electrolysis	chromate	40	A17	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention												
87	EG	electrolysis	chromate	40	A18	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention											
88	EG	electrolysis	chromate	40	A21	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention										
89	EG	electrolysis	chromate	40	A22	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention									
90	EG	electrolysis	chromate	40	A25	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention								
91	EG	electrolysis	chromate	40	A26	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention							
92	EG	electrolysis	chromate	40	A28	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention						
93	EG	electrolysis	chromate	40	A29	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention				
94	EG	electrolysis	chromate	40	A31	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention			
95	EG	electrolysis	chromate	40	A32	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention		
96	EG	electrolysis	chromate	40	A35	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
97	EG	electrolysis	chromate	40	A36	B1	20	C2	5	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention

Table 10

No.	Mat- erial	Substrate layer treatment		Solid composition of film				Coverage g/m ²	Film performance					Note		
		Treatment method	Type	Coverage mg/m ²	Polymer type	Silica			Wax		Corrosion resistance	Coating adhe- sion	Solvent resistance EtOH MEK		Press galling resist- ance	Weld- abil- ity
						Type	Amount		Type	Amount						
98	EG	electrolysis	chromate	40	A1	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
99	EG	electrolysis	chromate	40	A2	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
100	EG	electrolysis	chromate	40	A3	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
101	EG	electrolysis	chromate	40	A4	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
102	EG	electrolysis	chromate	40	A5	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
103	EG	electrolysis	chromate	40	A6	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
104	EG	electrolysis	chromate	40	A7	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
105	EG	electrolysis	chromate	40	A9	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
106	EG	electrolysis	chromate	40	A10	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
107	EG	electrolysis	chromate	40	A13	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
108	EG	electrolysis	chromate	40	A14	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
109	EG	electrolysis	chromate	40	A17	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
110	EG	electrolysis	chromate	40	A18	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
111	EG	electrolysis	chromate	40	A21	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
112	EG	electrolysis	chromate	40	A22	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
113	EG	electrolysis	chromate	40	A25	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
114	EG	electrolysis	chromate	40	A26	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
115	EG	electrolysis	chromate	40	A28	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
116	EG	electrolysis	chromate	40	A29	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
117	EG	electrolysis	chromate	40	A31	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
118	EG	electrolysis	chromate	40	A32	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
119	EG	electrolysis	chromate	40	A35	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	
120	EG	electrolysis	chromate	40	A36	B1	20	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Invention	

Table 11

No.	Mat- erial	Substrate layer treatment		Solid composition of film						Coverage g/m ²	Film performance					Note
		Treatment method	Type	Coverage mg/m ²	Polymer type	Silica		Wax			Corrosion resistance	Coating adhe- sion	Solvent resistance EtOH MEK	Press galling resist- ance	Weld- abil- ity	
						Type	Amount	Type	Amount							
121	EG	electrolysis	chromate	40	A1	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
122	EG	electrolysis	chromate	40	A2	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
123	EG	electrolysis	chromate	40	A3	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
124	EG	electrolysis	chromate	40	A4	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
125	EG	electrolysis	chromate	40	A5	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
126	EG	electrolysis	chromate	40	A6	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
127	EG	electrolysis	chromate	40	A7	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
128	EG	electrolysis	chromate	40	A9	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
129	EG	electrolysis	chromate	40	A10	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
130	EG	electrolysis	chromate	40	A13	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
131	EG	electrolysis	chromate	40	A14	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
132	EG	electrolysis	chromate	40	A17	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
133	EG	electrolysis	chromate	40	A18	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
134	EG	electrolysis	chromate	40	A21	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
135	EG	electrolysis	chromate	40	A22	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
136	EG	electrolysis	chromate	40	A25	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
137	EG	electrolysis	chromate	40	A26	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
138	EG	electrolysis	chromate	40	A28	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
139	EG	electrolysis	chromate	40	A29	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
140	EG	electrolysis	chromate	40	A31	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
141	EG	electrolysis	chromate	40	A32	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
142	EG	electrolysis	chromate	40	A35	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
143	EG	electrolysis	chromate	40	A36	B1	20	C1	1	⊙	⊙	⊙	⊙	⊙	Invention	
144	EG	electrolysis	chromate	40	A1	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
145	EG	electrolysis	chromate	40	A2	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
146	EG	electrolysis	chromate	40	A3	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
147	EG	electrolysis	chromate	40	A4	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
148	EG	electrolysis	chromate	40	A5	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
149	EG	electrolysis	chromate	40	A6	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
150	EG	electrolysis	chromate	40	A7	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
151	EG	electrolysis	chromate	40	A9	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	
152	EG	electrolysis	chromate	40	A10	B1	20	C2	1	⊙	⊙	⊙	⊙	⊙	Invention	

Table 12

No.	Mat- erial	Substrate layer treatment		Solid composition of film					Coverage g/m ²	Film performance					Note
				Treatment method	Type	Coverage mg/m ²	Polymer type	Silica		Wax					
		Type	Amount					Type	Amount	Corrosion resistance	Coating adhe- sion	Solvent resistance	Press galling resist- ance	Weld- ing abil- ity	
		Flat sec- tion	Drawn section	EtOH	MEK	MEK									
153	EG	electrolysis	chromate	40	A13	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
154	EG	electrolysis	chromate	40	A14	B1	20	C2	1	1.0	○	○	○	○	Invention
155	EG	electrolysis	chromate	40	A17	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
156	EG	electrolysis	chromate	40	A18	B1	20	C2	1	1.0	○	○	○	○	Invention
157	EG	electrolysis	chromate	40	A21	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
158	EG	electrolysis	chromate	40	A22	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
159	EG	electrolysis	chromate	40	A25	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
160	EG	electrolysis	chromate	40	A26	B1	20	C2	1	1.0	○	○	○	○	Invention
161	EG	electrolysis	chromate	40	A28	B1	20	C2	1	1.0	○	○	○	○	Invention
162	EG	electrolysis	chromate	40	A29	B1	20	C2	1	1.0	○	○	○	○	Invention
163	EG	electrolysis	chromate	40	A31	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
164	EG	electrolysis	chromate	40	A32	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
165	EG	electrolysis	chromate	40	A35	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
166	EG	electrolysis	chromate	40	A36	B1	20	C2	1	1.0	⊙	⊙	⊙	⊙	Invention
167	EG	electrolysis	chromate	40	A1	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
168	EG	electrolysis	chromate	40	A2	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
169	EG	electrolysis	chromate	40	A3	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
170	EG	electrolysis	chromate	40	A4	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
171	EG	electrolysis	chromate	40	A5	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
172	EG	electrolysis	chromate	40	A6	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
173	EG	electrolysis	chromate	40	A7	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
174	EG	electrolysis	chromate	40	A9	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
175	EG	electrolysis	chromate	40	A10	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
176	EG	electrolysis	chromate	40	A13	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
177	EG	electrolysis	chromate	40	A14	B1	20	C3	1	1.0	○	○	○	○	Invention
178	EG	electrolysis	chromate	40	A17	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
179	EG	electrolysis	chromate	40	A18	B1	20	C3	1	1.0	○	○	○	○	Invention
180	EG	electrolysis	chromate	40	A21	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
181	EG	electrolysis	chromate	40	A22	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
182	EG	electrolysis	chromate	40	A25	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
183	EG	electrolysis	chromate	40	A26	B1	20	C3	1	1.0	○	○	○	○	Invention
184	EG	electrolysis	chromate	40	A28	B1	20	C3	1	1.0	○	○	⊙	⊙	Invention
185	EG	electrolysis	chromate	40	A29	B1	20	C3	1	1.0	○	○	⊙	⊙	Invention
186	EG	electrolysis	chromate	40	A31	B1	20	C3	1	1.0	⊙	⊙	○	○	Invention
187	EG	electrolysis	chromate	40	A32	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
188	EG	electrolysis	chromate	40	A35	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention
189	EG	electrolysis	chromate	40	A36	B1	20	C3	1	1.0	⊙	⊙	⊙	⊙	Invention

As seen in Tables 7 to 12, all of the surface-treated metal sheets obtained by the surface treatment method of the invention clearly exhibited not only excellent corrosion resistance of flat test pieces, solvent resistance, top coatability and weldability, but also excellent corrosion resistance after Erichsen drawing and scratch resistance.

Industrial Applicability

Since the surface-treated metal sheets of the invention exhibit not only excellent corrosion resistance of flat test pieces, solvent resistance, top coatability and weldability, but also excellent corrosion resistance after Erichsen drawing and scratch resistance, they are suitable as materials for the fields of electrical appliances, construction materials and automobiles, and therefore offer very high value for use in industry. Moreover, the aqueous surface treatment agent and surface-treated metal sheet production process of the invention are able to provide to the market surface-treated metal sheets with excellent corrosion resistance of flat test pieces, solvent resistance, top coatability, weldability, corrosion resistance after Erichsen drawing and scratch resistance.

CLAIMS

1. An aqueous surface treatment agent characterized by comprising an acrylic-based resin, water and 5-35 wt% of colloidal silica in terms of solid weight, wherein said acrylic-based resin is a polymer obtained by polymerization reaction of, in terms of solid weight, (a) 15-76 wt% of a (meth)acrylate unsaturated monomer represented by the following general formula (1):



where R^1 is hydrogen or methyl and R^2 is a linear or branched alkyl of 1-8 carbons, (b) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a carboxyl group in the molecule, (c) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a hydroxyl group in the molecule, (d) 10-30 wt% of styrene, (e) 10-30 wt% of acrylonitrile and (f) 0-10 wt% of an unsaturated monomer which is polymerizable with these monomers, and wherein the acrylic-based resin has a glass transition temperature of 0-30°C.

2. An aqueous surface treatment agent according to claim 1, characterized in that (f) in said acrylic-based resin includes an unsaturated monomer having at least one functional group selected from among glycidyl, aziridiny, methylol and silanol in the molecule.

3. An aqueous surface treatment agent according to claim 1 or 2, characterized in that the aqueous surface treatment agent contains a polyolefin wax dispersion at no more than 35 wt% in terms of solid weight.

4. A surface-treated metal material characterized in that it has 0.3-5.0 g/m² of an organic/inorganic composite film comprising an acrylic-based resin and 5-35 wt% of colloidal silica in terms of solid weight on a plated metal sheet, said acrylic-based resin being a

polymer obtained by polymerization reaction of, in terms of solid weight, (a) 15-76 wt% of a (meth)acrylate unsaturated monomer represented by the following general formula (1):



where R^1 is hydrogen or methyl and R^2 is a linear or branched alkyl of 1-8 carbons, (b) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a carboxyl group in the molecule, (c) 2-10 wt% of an α,β -ethylenic unsaturated monomer with a hydroxyl group in the molecule, (d) 10-30 wt% of styrene, (e) 10-30 wt% of acrylonitrile and (f) 0-10 wt% of an unsaturated monomer which is polymerizable with these monomers, and the acrylic-based resin having a glass transition temperature of 0-30°C.

5. A surface-treated metal material according to claim 4, characterized in that (f) in said acrylic-based resin includes an unsaturated monomer having at least one functional group selected from among glycidyl, aziridinyl, methylol and silanol in the molecule.

6. A surface-treated metal material according to claim 4 or 5, characterized in that the aqueous surface treatment agent contains a polyolefin wax dispersion at no more than 35 wt% in terms of solid weight.

7. A process for production of a surface-treated metal material, characterized by coating an aqueous surface treatment agent according to any one of claims 1 to 3 onto a plated metal sheet or a surface-prepared plated metal sheet at 0.3-5.0 g/m² in terms of dry solid weight, and then drying it to form an organic/inorganic composite film.