

Description

Title of Invention

SURFACE-TREATED STEEL SHEET

5

Technical Field

[0001]

The present invention relates to a surface-treated steel sheet having a dry coating film on a surface.

10

Background Art

[0002]

Conventionally, zinc-plated steel sheets are used in various fields such as home electrical appliances, building materials, and automobiles. As a method for improving the corrosion resistance etc. of a zinc-plated steel sheet, a technology in which a dry coating film is formed on a surface of the zinc-plated steel sheet is widely used (for example, see Patent Literature 1 to Patent Literature 6).

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Citation List

20 Patent Literature

[0003]

Patent Literature 1: JP 2011-183307A

Patent Literature 2: JP 2003-13252A

Patent Literature 3: JP 5642082B

25 Patent Literature 4: JP 2012-92444A

Patent Literature 5: WO 2011/122119

Patent Literature 6: JP 2011-225967A

Summary of Invention

30 Technical Problem

[0004]

Important required characteristics regarding the external appearance quality of a surface of a surface-treated steel sheet used in a non-coating form include water condensation whitening resistance. Water condensation whitening (white rust) is a phenomenon in which a contact portion with condensation water that has occurred on a surface of a surface-treated steel sheet whitens. However, a conventional zinc-plated steel sheet having a dry coating film on a surface has been unable to sufficiently suppress water condensation whitening. In addition, still further improvement in corrosion resistance has been required of the conventional zinc-plated steel sheet having a dry coating film on a surface.

10 [0005]

The present invention has been made in view of such circumstances, and an issue of the present invention is to provide a surface-treated steel sheet having excellent water condensation whitening resistance and corrosion resistance.

15 Solution to Problem

[0006]

The present inventors conducted extensive studies in order to solve the issue mentioned above. The present inventors first conducted studies on components that constitute a dry coating film, and have found that a dry coating film formed using a treatment agent containing P, Ti, V, Si, and a polyurethane resin improves water condensation whitening resistance and corrosion resistance.

[0007]

Further, the present inventors focused attention on the possibility that water condensation whitening resistance and corrosion resistance will be further improved by preparing a polyurethane resin in a fine particle form, dispersing the particles in a dry coating film uniformly, and thereby dispersing components having corrosion suppression action, such as V and Ti, in the dry coating film uniformly. Then, the present inventors employed a special production method that uses acetic acid as a component of a treatment agent, and consequently observed a dry coating film in which a polyurethane resin is dispersed uniformly in a particle form in the composition system mentioned above for the first time. In addition, surprisingly,

the present inventors have found that the dry coating film thus formed not only exhibits excellent water condensation whitening resistance and corrosion resistance, but also exhibits high resistance to stacking whitening that occurs in an environment quite different from the environment of water condensation whitening.

5 The gist of the present invention is as follows.

[0008]

(1)

A surface-treated steel sheet including:

a steel sheet;

10 a plating layer containing zinc and formed on a surface of the steel sheet;
and

a dry coating film formed on the plating layer,

in which the dry coating film contains a resin component containing resin particles made of a polyurethane resin with an average particle size of more than or
15 equal to 20 nm and less than or equal to 200 nm, P, Ti, V, and Si,

the dry coating film contains P at more than or equal to 2.5 mass% and less than or equal to 7.5 mass% on a phosphoric acid basis,

an area ratio of the resin component in a cross section of the dry coating film is more than or equal to 35% and less than or equal to 80%,

20 the resin particles are dispersed in the dry coating film, and

a maximum value of a distance between centers of gravity of resin particles is less than or equal to 3.0 times an average particle size of the resin particle.

[0009]

(2)

25 The surface-treated steel sheet according to (1),

in which a surface roughness (Ra) of the dry coating film is more than or equal to 1 nm and less than or equal to 10 nm.

(3)

The surface-treated steel sheet according to (1) or (2),

30 in which a surface roughness (Ra) of the steel sheet is more than or equal to 0.1 μm and less than or equal to 2 μm .

(4)

The surface-treated steel sheet according to any one of (1) to (3),
in which the plating layer contains antimony.

(5)

5 The surface-treated steel sheet according to any one of (1) to (4),
in which the resin component contains olefin-based wax and/or a phenolic
resin.

[0010]

(6)

10 The surface-treated steel sheet according to any one of (1) to (5),
in which the dry coating film contains

Si at more than or equal to 10 mass% and less than or equal to 40
mass% on a SiO₂ basis,

15 Ti at more than or equal to 1.7 mass% and less than or equal to 2.4
mass%, and

V at more than or equal to 0.70 mass% and less than or equal to
0.90 mass%, and

a mass ratio between Ti and V (Ti/V) is more than or equal to 2.1 and less
than or equal to 2.9.

20

Advantageous Effects of Invention

[0011]

As above, the surface-treated steel sheet of the present invention has
excellent water condensation whitening resistance and corrosion resistance.

25 [0012]

Further, surprisingly, the surface-treated steel sheet of the present invention
has also more excellent stacking whitening resistance by virtue of having the above
configuration. Here, "stacking whitening resistance" refers to corrosion resistance
when a coil or the like of a surface-treated steel sheet is transported and stored in a
30 high-temperature, high-humidity environment. In stacking whitening, the
temperature that controls the reaction rate is high and the amount of water, which is a

reaction field, is small; on the other hand, water condensation whitening is different in that the temperature is normal temperature and the amount of water, which is a reaction field, is large; thus, the fact that both resistances have been improved successfully is a surprising effect.

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Brief Description of Drawings

[0013]

[FIG. 1] FIG. 1 is a schematic diagram for describing an example of a cross-sectional structure of a surface-treated steel sheet of the present embodiment.

10 [FIG. 2] FIG. 2 is a schematic cross-sectional view of a dry coating film for describing a method for comparing a distance between centers of gravity of resin particles and an average particle size of a resin particle.

[FIG. 3] FIG. 3 is a schematic cross-sectional view of a dry coating film for describing a method for comparing a distance between centers of gravity of resin
15 particles and an average particle size of a resin particle.

[FIG. 4] FIG. 4 is a bright field (STEM-BF) image obtained by observing a cross section of a surface-treated steel sheet of Example 4 with a scanning transmission electron microscope (STEM).

[FIG. 5] FIG. 5 is a high-angle annular dark field (STEM-HAADF) image obtained
20 by observing a cross section of a surface-treated steel sheet of Example 4 with a scanning transmission electron microscope (STEM).

[FIG. 6] FIG. 6 is a high-angle annular dark field (STEM-HAADF) image obtained by observing a cross section of a surface-treated steel sheet of Example 4 with a scanning transmission electron microscope (STEM).

25 [FIG. 7] FIG. 7 is a bright field (STEM-BF) image obtained by observing a cross section of a surface-treated steel sheet of Comparative Example 11 with a scanning transmission electron microscope (STEM).

[FIG. 8] FIG. 8 is a bright field (STEM-BF) image obtained by observing a cross
30 section of a surface-treated steel sheet of Comparative Example 11 with a scanning transmission electron microscope (STEM).

Description of Embodiments

[0014]

Hereinafter, (a) preferred embodiment(s) of the present disclosure will be described in detail with reference to the appended drawings. Note that, in this specification and the appended drawings, structural elements that have substantially the same function and structure are denoted with the same reference numerals, and repeated explanation of these structural elements is omitted. Further, in the present specification, the description of the numerical range of "a to b" is a description intending to include not only the range between a and b but also the upper limit value and the lower limit value. That is, in the present specification, the description of "a to b" should be construed as meaning "more than or equal to a and less than or equal to b."

[0015]

1. Surface-treated steel sheet

FIG. 1 is a schematic diagram for describing an example of a cross-sectional structure of a surface-treated steel sheet of the present embodiment.

A surface-treated steel sheet 10 shown in FIG. 1 includes a steel sheet 1, a plating layer 2 containing zinc and formed on a surface 1a of the steel sheet 1, and a dry coating film 3 formed on the plating layer 2.

Although the surface-treated steel sheet 10 shown in FIG. 1 is described using, as an example, a case where the plating layer 2 and the dry coating film 3 are formed only on the side of one surface 1a of the steel sheet 1, the surface-treated steel sheet of the present invention may have a configuration in which plating layers and dry coating films are formed on both surfaces of a steel sheet. Further, in the case where plating layers 2 are formed on both surfaces of the steel sheet 1, the dry coating film 3 may be formed only on one surface, or may be formed on both surfaces.

[0016]

1.1 Steel sheet

In the present embodiment, the steel sheet 1 in which the plating layer 2 is formed on the surface 1a is not particularly limited. For example, as the steel sheet

1, any type of steel sheet may be used, such as an ultra-low C type (a ferrite-based structure), an Al-k type (a structure containing pearlite in ferrite), a two-phase structure type (for example, a structure containing martensite in ferrite or a structure containing bainite in ferrite), a processing-induced transformation type (a structure containing residual austenite in ferrite), or a fine crystal type (a ferrite-based structure).

[0017]

The surface roughness Ra of the steel sheet 1 (test length: 1 inch) (hereinafter, occasionally referred to as "Ra-S") is not particularly limited, but is preferably 0.1 to 2 μm . In the dry coating film 3, the distribution of each component in the dry coating film 3 is uniform as a result of a polyurethane resin being dispersed uniformly, and hence the diffuse reflection of injected light in the dry coating film 3 is relatively suppressed. Further, in the dry coating film 3, excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are exhibited even in the case of a relatively small film thickness, for example, a thickness of 500 nm. In the case where components are thus uniformly distributed in the dry coating film 3 and the film thickness is relatively small, there is a case where an interference pattern occurs on the surface-treated steel sheet 10 depending on the composition etc. of the dry coating film 3.

[0018]

In this regard, the present inventors have found that an interference pattern is suppressed by setting the roughness of the surface of the steel sheet 1 within a prescribed range and thereby controlling the shape of the reflection interface on the plating layer 2 side of the dry coating film 3. Specifically, when the surface roughness (Ra-S) of the steel sheet 1 (test length: 1 inch) is more than or equal to 0.1 μm , an event in which an interference pattern is exhibited on the surface-treated steel sheet 10 can be avoided, and a good external appearance is obtained. The surface roughness (Ra-S) of the steel sheet 1 is more preferably more than or equal to 0.2 μm , and still more preferably more than or equal to 0.3 μm .

[0019]

On the other hand, when the surface roughness (Ra-S) of the steel sheet 1

(test length: 1 inch) is less than or equal to 2 μm , an event in which part of the steel sheet 1 pierces the dry coating film 3 and is exposed due to a large surface roughness of the steel sheet 1 can be prevented more reliably. Therefore, excellent corrosion resistance is obtained more reliably. The surface roughness (Ra-S) of the steel sheet 1 is more preferably less than or equal to 1.5 μm , and still more preferably less than or equal to 1.0 μm .

The surface roughness (Ra-S) of the steel sheet 1 (test length: 1 inch) is defined as the surface roughness (Ra) on the surface of the dry coating film 3 of the surface-treated steel sheet 10 in which the plating layer 2 and the dry coating film 3 are formed on the surface 1a of the steel sheet 1. In the present specification, the surface roughness Ra is obtained by measurement in accordance with JIS B 0601.

[0020]

1.2 Plating layer

The plating layer 2 contains zinc, and is formed on one surface or both surfaces of the steel sheet 1. The meaning of the plating layer containing zinc includes a pure zinc-based plating layer and a zinc alloy plating layer in which the zinc content is more than or equal to 40 mass%. Examples of the zinc alloy plating layer include a 55% Al-Zn alloy plating layer, a 5% Al-Zn alloy plating layer, an Al-Mg-Zn alloy plating layer, a Ni-Zn alloy plating layer, and the like.

20 [0021]

The plating layer 2 may contain antimony. In the plating layer 2 containing antimony, the corrosion resistance of the surface-treated steel sheet 10 tends to be low as compared to the case of not containing antimony. In the present embodiment, even when the plating layer 2 contains antimony, excellent water condensation whitening resistance, stacking whitening resistance, and corrosion resistance are obtained by virtue of the dry coating film 3 formed on the plating layer 2.

The attached amount of plating of the plating layer 2 is not particularly limited, and may be within a conventional ordinary range.

30 [0022]

1.3 Dry coating film

The dry coating film 3 is formed on the plating layer 2.

As shown in FIG. 1, the dry coating film 3 is composed of a first component 31 (a resin component) that contains resin particles made of a polyurethane resin with an average particle size of 20 to 200 nm and a second component 32 excluding
5 the first component 31. The area ratio of the first component 31 in a cross section of the dry coating film 3 is 35 to 80%. The second component 32 contains phosphorus (P), titanium (Ti), vanadium (V), and silicon (Si). In the dry coating film 3, P is contained at 2.5 to 7.5 mass% on a phosphoric acid basis. In the dry coating film 3, the first component 31 and the second component 32 are dispersed
10 substantially uniformly.

[0023]

The dry coating film 3 is obtained by applying, on the plating layer 2, a water-based surface treatment agent containing the components to be contained in the dry coating film 3 at a prescribed ratio and drying the water-based surface
15 treatment agent. A mechanism by which the dry coating film 3 of the present embodiment is formed will now be described.

[0024]

When a water-based surface treatment agent containing the components to be contained in the dry coating film 3 at a prescribed ratio is applied on the plating
20 layer 2, phosphorus (P) in the water-based surface treatment agent is deposited on the surface of the plating layer 2, and a wet coating film in which the first component 31 (resin component) is dispersed substantially uniformly in a self-aligned manner is formed. It is inferred that this is due to the fact that the balance between the surface energy of the water-based surface treatment agent and the surface energy of the
25 plating layer 2 on which phosphorus in the water-based surface treatment agent is deposited and the balance of the specific gravity of the first component 31 existing in the water-based surface treatment agent are appropriate. It is inferred that, when a wet coating film obtained by applying the water-based surface treatment agent is dried, a dry coating film 3 in which the first component 31 and the second
30 component 32 existing between adjacent particles of the first component 31 are arranged substantially uniformly is formed while a substantially uniform dispersion

state of the first component 31 in the wet coating film is maintained.

[0025]

As described later, in the present embodiment, the water-based surface treatment agent contains an acetic acid component. The acetic acid component can stabilize the pH of the water-based surface treatment agent by pH buffer action. It is presumed that, in the water-based surface treatment agent, the acetic acid component suppresses and stabilizes the condensation reaction of a precursor of silicon (Si), such as a silane coupling agent, and consequently contributes to the suppression of aggregation and association of resin particles of the first component. By the acetic acid component thus stabilizing each component of the water-based surface treatment agent, also in the formed dry coating film 3 the first component 31 is allowed to exist as relatively uniform, fine resin particles. In contrast, in the case where the water-based surface treatment agent does not contain the acetic acid component, each component of such a water-based surface treatment agent is not stabilized, and consequently the first component cannot disperse uniformly or finely in the formed dry coating film.

[0026]

In the dry coating film 3 in which the first component 31 and the second component 32 are dispersed substantially uniformly, the effect of improving corrosion resistance, water condensation whitening resistance, and stacking whitening resistance based on the first component 31 and the second component 32 is obtained substantially uniformly in the entire plane of the dry coating film. As a result, in the surface-treated steel sheet 10 of the present embodiment, excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are obtained. Although the principle of the exhibition of such an effect is not certain, an inferred mechanism of the exhibition of the effect will now be described.

[0027]

That is, first, the dry coating film 3 is formed uniformly by film production action based on the first component 31 and silicon contained in the second component 32, and excellent barrier properties and adhesiveness are exhibited.

Hence, in any place of the dry coating film 3, the entry of water, oxygen, etc. can be suppressed, and the seepage of each component of the surface-treated steel sheet 10 from the dry coating film 3 onto the surface of the dry coating film 3 is suppressed. As a result, by the dry coating film 3, corrosion resistance is improved, and water
5 condensation whitening resistance and stacking whitening resistance are improved.

[0028]

On the other hand, titanium (Ti) and vanadium (V) are distributed substantially uniformly in the entire plane of the dry coating film 3; hence, even when corrosion has started in part of the surface-treated steel sheet 10, these
10 components can access the portion quickly, and corrosion can be suppressed. Further, since titanium (Ti) and vanadium (V) are distributed substantially uniformly in the entire plane of the dry coating film 3, even when titanium (Ti) and vanadium (V) have become lacking in part of the surface-treated steel sheet 10, titanium (Ti) and vanadium (V) are supplied to the portion quickly.

15 [0029]

Excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are obtained by the synergy of film production action based on the first component 31 and silicon (Si) contained in the second component 32 and corrosion suppression action based on titanium (Ti) and vanadium (V).

20 [0030]

In the present embodiment, the dispersion state of the first component 31 in the dry coating film 3 is evaluated using the maximum value of the distance between the centers of gravity of resin particles. In the present embodiment, the maximum value of the distance between the centers of gravity of resin particles is less than or
25 equal to 3.0 times the average particle size, more preferably less than or equal to 2.5 times, and still more preferably less than or equal to 2.0 times. When the maximum value of the distance between the centers of gravity of resin particles is less than or equal to 3.0 times, the effect by the first component 31 and the second component 32 being uniformly arranged in the dry coating film 3 is high, and a surface-treated steel
30 sheet 10 excellent in corrosion resistance, water condensation whitening resistance, and stacking whitening resistance is obtained. On the other hand, the maximum

value of the distance between the centers of gravity of resin particles is preferably more than 1.0 time the average particle size, more preferably more than or equal to 1.25 times, and still more preferably more than or equal to 1.5 times in order to achieve both a sufficiently excellent effect of improving barrier properties and adhesiveness based on the first component 31 and a sufficiently excellent effect of improving corrosion resistance based on the second component 32.

[0031]

The maximum value of the distance between the centers of gravity of resin particles in the dry coating film 3 can be found in the following way.

First, resin particles are identified in the cross sections of arbitrary three places of the first component 31 of the dry coating film 3, which cross sections are obtained by carbon element mapping of cross-sectional transmission electron microscopy-energy dispersive X-ray spectrometry (TEM-EDX) or a scanning TEM-high-angle annular dark field (STEM-HAADF) image, and the outline of the resin particle is taken as the outermost side of the resin particle. In the case where the resin particle of the measurement object is a substantially perfect circle, the particle size and the center of gravity of the resin particle are taken as the particle size and the center of gravity themselves of the resin particle. In the case where the resin particle of the measurement object is not a perfect circle, the maximum diameter and the minimum diameter of the resin particle are measured, and the cross section of the resin particle is regarded as an ellipse having the maximum diameter and the minimum diameter as the major axis and the minor axis, respectively. Then, the area of the ellipse is calculated, and the particle size and the center of gravity of the resin particle are determined on the assumption that the resin particle is a perfect circle having the calculated area and having the center of gravity at a point at which the maximum diameter and the minimum diameter cross.

[0032]

Then, the maximum value of the distance between the centers of gravity of resin particles that are mutually adjacent and yet not mutually in contact (the distance between the centers in the case where the cross-sectional shape of each resin particle is regarded as a circular shape) is calculated in each of the cross sections of three

places of the first component 31 in the cross section of the dry coating film 3; and the average value of the values obtained from the cross sections of three places is found, and is taken as the maximum value of the distance between the centers of gravity of resin particles.

5 The calculation of the center of gravity etc. mentioned above may be performed while the specific gravity of the interior of the resin particle is regarded as fixed.

[0033]

FIG. 2 and FIG. 3 are schematic cross-sectional views of dry coating films
10 for describing a method for comparing the distance between the centers of gravity of resin particles and the average particle size of the resin particle. FIG. 2 shows an example in which the maximum value of the distance between the centers of gravity of resin particles is less than or equal to 3.0 times the average particle size, and FIG. 3 shows an example in which the maximum value of the distance between the centers
15 of gravity of resin particles is more than 3.0 times the average particle size. A description of the plating layer and the steel sheet 1 is omitted.

In FIG. 2, first, the distance l between the centers of gravity of resin particles 311 that are mutually adjacent and yet not mutually in contact in the dry coating film 3 is found. Next, with comparison to the average particle size of the
20 resin particle 311, the ratio of the maximum value of the distance l between the centers of gravity of resin particles 311 to the average particle size is found. An imaginary resin particle 312 having the average particle size is shown by a broken line.

[0034]

25 In FIG. 3, first, the distance lA between the centers of gravity of resin particles 311A that are mutually adjacent and yet not mutually in contact in the dry coating film 3A is found. Next, with comparison to the average particle size of the resin particle 311A, the ratio of the maximum value of the distance lA between the centers of gravity of resin particles 311A to the average particle size is found. An
30 imaginary resin particle 312A having the average particle size is shown by a broken line.

[0035]

The smoothness of a surface 33 of the dry coating film 3 has a correlation with the dispersion state of resin particles 31 in the dry coating film 3. Thus, the dispersion state of resin particles in the dry coating film 3 can be evaluated also by using the surface roughness (Ra) of the dry coating film 3. Further, the dispersion state of resin particles in the dry coating film 3 may be evaluated using, together with the surface roughness (Ra) of the dry coating film 3 or instead of the surface roughness (Ra) of the dry coating film 3, the maximum cross-sectional height (Rt) and/or the root-mean-square roughness (Rq) of a roughness curve.

10 [0036]

The surface roughness (Ra) of the dry coating film 3 (hereinafter, occasionally referred to as "Ra-F") is preferably 1 to 10 nm. When the surface roughness (Ra-F) of the dry coating film 3 is more than or equal to 1 nm, the dry coating film 3 can be produced easily, and is excellent in productivity. When the surface roughness (Ra-F) of the dry coating film 3 is less than or equal to 10 nm, the effect by the first component 31 and the second component 32 being uniformly arranged in the dry coating film is even higher, and a surface-treated steel sheet 10 more excellent in corrosion resistance, water condensation whitening resistance, and stacking whitening resistance is obtained. The surface roughness (Ra-F) of the dry coating film 3 is preferably less than or equal to 5 nm.

[0037]

For a reason similar to the reason why it is preferable for the surface roughness (Ra-F) of the dry coating film 3 to be 1 to 10 nm, the maximum cross-sectional height (Rt) of a roughness curve of the dry coating film 3 is preferably 20 to 200 nm, and the root-mean-square roughness (Rq) of the dry coating film 3 is more preferably 1 to 10 nm. The arithmetic average roughness (Ra), the maximum cross-sectional height (Rt), and the root-mean-square roughness (Rq) may be calculated from measurement data that are obtained by using an atomic force microscope to scan an arbitrary rectangular region having four 1- μ m sides.

30 [0038]

The area ratio of the first component 31 (resin component) in a cross section

of the dry coating film 3 is 35 to 80%. In the present embodiment, since the area ratio of the first component 31 of the dry coating film 3 is more than or equal to 35%, a dry coating film formation function based on the first component 31 is obtained sufficiently, and a dry coating film 3 excellent in barrier properties and adhesiveness is obtained. Thus, a surface-treated steel sheet 10 excellent in corrosion resistance, water condensation whitening resistance, and stacking whitening resistance is obtained. The area ratio of the first component 31 is preferably more than or equal to 40% in order to improve the effect of improving barrier properties and adhesiveness based on the first component 31 even more. Further, in the present embodiment, since the area ratio of the first component 31 of the dry coating film 3 is less than or equal to 80%, the effect of improving corrosion resistance based on the second component 32 is obtained sufficiently, and excellent corrosion resistance is obtained. The area ratio of the first component 31 is preferably less than or equal to 60% in order to improve the effect of improving corrosion resistance based on the second component 32 even more.

[0039]

The area ratio of the first component 31 (resin component) in a cross section of the dry coating film 3 can be obtained in the following way.

First, a carbon film is vapor-deposited as a protection film on a surface of the surface-treated steel sheet 10, and a carbon film of several micrometers is formed using a focused ion beam processing apparatus (FIB). After that, a FIB is used to perform microsampling at an acceleration voltage of 30 kV (finish processing: 5 kV), and the sample is made into a thin film to obtain a sample of a cross section of the dry coating film 3. The obtained sample is observed using a transmission electron microscope (TEM) or a scanning electron microscope (SEM) having an energy dispersive X-ray spectroscopy (EDS); for the dry coating film 3 of each surface-treated steel sheet 10, EDS analysis (element mapping) of the cross sections of three places is performed, and maps of the elements of C, P, Ti, V, and Si are obtained. The obtained element map is divided into 100 squares (10×10) and is binarized into C and the other elements, and the area ratio of the resin component in the cross section of the dry coating film is calculated.

[0040]

The thickness of the dry coating film 3 is preferably 150 to 900 nm, but is not limited to this. When the thickness of the dry coating film 3 is 150 to 900 nm, the effect of improving corrosion resistance based on the dry coating film 3 is noticeable, and even more excellent corrosion resistance is obtained.

[0041]

The first component 31 and the second component 32 that constitute the dry coating film 3 will now be described in detail.

(i) First component

The first component 31 contains resin particles made of a polyurethane resin with an average particle size of 20 to 200 nm. The polyurethane resin forms a dry coating film having a good balance between tensile strength and extension. Hence, the dry coating film 3 containing the first component 31 containing a polyurethane resin is excellent in barrier properties and adhesiveness. Thus, the surface-treated steel sheet 10 of the present embodiment has excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance.

[0042]

The contained amount of the polyurethane resin in the dry coating film 3 is preferably 25 to 45 mass%. When the contained amount of the polyurethane resin is more than or equal to 25 mass% and more preferably more than or equal to 30 mass%, a dry coating film 3 in which the effect of improving barrier properties and adhesiveness based on the polyurethane resin is obtained more effectively is obtained. When the contained amount of the polyurethane resin is less than or equal to 45 mass% and more preferably less than or equal to 40 mass%, the contained amounts of the other components can be ensured sufficiently, and therefore more excellent corrosion resistance is obtained.

[0043]

If the average particle size of the polyurethane resin is less than 20 nm, resin particles made of the polyurethane resin are likely to aggregate, and resin particles are less likely to disperse uniformly in the dry coating film 3. Consequently, there is a concern that a dry coating film 3 in which resin particles are arranged to exist

locally will be obtained, and the corrosion resistance, water condensation whitening resistance, and stacking whitening resistance of the surface-treated steel sheet 10 will be insufficient. In the present embodiment, since the average particle size of the polyurethane resin is more than or equal to 20 nm, excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are obtained. When the average particle size of the polyurethane resin is more than or equal to 50 nm, even more excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are obtained. Further, in the present embodiment, since the average particle size of the polyurethane resin is less than or equal to 200 nm, a dry coating film 3 in which resin particles are dispersed substantially uniformly is formed by forming the dry coating film 3 by a method described later. The average particle size of the polyurethane resin is more preferably less than or equal to 100 nm.

[0044]

The average particle size of the resin particle made of a polyurethane resin in the dry coating film can be calculated by a method of observing a cross section of the dry coating film shown below. First, a carbon film is vapor-deposited as a protection film on a surface of a steel sheet. Subsequently, a carbon film of several micrometers is formed using a focused ion beam processing apparatus (FIB), SMI3050SE, manufactured by Hitachi High-Tech Science Corporation. After that, a FIB is used to perform microsampling at an acceleration voltage of 30 kV (finish processing: 5 kV), and the sample is made into a thin film to obtain a sample of a cross section of the dry coating film. The obtained sample is observed using a transmission electron microscope (TEM) or a scanning electron microscope (SEM). 10 resin particles each having a large circle-equivalent diameter are selected from the observed resin particles, and the average value of the diameters is taken as the average particle size of the resin particle made of a polyurethane resin.

A study by the present inventors has shown that, in the present embodiment, the result of the average particle size of the resin particle made of a polyurethane resin calculated by the method mentioned above substantially coincides with the average particle size of a polyurethane resin used as a material of the water-based

surface treatment agent. Thus, the average particle size of the resin particle made of a polyurethane resin in the dry coating film can be regarded as the same as the average particle size of a polyurethane resin used as a material of the water-based surface treatment agent.

5 [0045]

The first component 31 (resin component) may contain not only polyurethane resin particles but also olefin-based wax and/or a phenolic resin.

Olefin-based wax is contained as necessary, and may not be contained. Olefin-based wax is preferably contained in the resin component in order to impart
10 lubricity to the dry coating film 3. Examples of the olefin-based wax include polyethylene wax, polyethylene oxide wax, polypropylene oxide wax, and the like. The olefin-based wax is preferably resin particles with an average particle size of 20 to 200 nm.

[0046]

15 In the case where the first component 31 contains olefin-based wax, the contained amount of olefin-based wax in the dry coating film 3 is preferably 3.5 to 6.0 mass%. When the contained amount of olefin-based wax is more than or equal to 3.5 mass% and more preferably more than or equal to 4.0 mass%, a dry coating film 3 in which the effect of improving lubricity based on the olefin-based wax is
20 obtained sufficiently is obtained, and a surface-treated steel sheet 10 having excellent processability is obtained. When the contained amount of olefin-based wax is less than or equal to 6.0 mass% and more preferably less than or equal to 5.5 mass%, the contained amounts of the other components can be ensured sufficiently, and therefore more excellent corrosion resistance is obtained.

25 [0047]

The first component 31 may contain a phenolic resin, as necessary. When a phenolic resin is contained in the dry coating film 3, the adhesiveness of the dry coating film 3 is improved even more.

[0048]

30 (ii) Second component

The second component 32 contains P, Ti, V, and Si.

Phosphorus (P) contained in the second component 32 suppresses, in the dry coating film 3, an event in which zinc, which is a cause of white rust, dissolves out from the plating layer 2, and suppresses the occurrence of white rust.

[0049]

5 The P content in the dry coating film 3 is 2.5 to 7.5 mass% on a phosphoric acid basis. A dry coating film 3 in which the P content in the dry coating film 3 is more than or equal to 2.5 mass% on a phosphoric acid basis is formed using a water-based surface treatment agent containing phosphorus sufficiently. Therefore, at the stage when the water-based surface treatment agent is applied on the plating layer 2,
10 phosphorus in the water-based surface treatment agent is deposited on the surface of the plating layer 2, and the surface energy of the plating layer 2 becomes appropriate; thus, a wet coating film in which the first component 31 is dispersed substantially uniformly in a self-aligned manner is formed. As a result, by drying the wet coating film, a dry coating film 3 in which the first component 31 and the second component
15 32 are arranged substantially uniformly is formed. In the present embodiment, since the P content in the dry coating film 3 is more than or equal to 2.5 mass%, good stacking whitening resistance and filament tape resistance are obtained. The P content in the dry coating film 3 is preferably more than or equal to 3.0 mass% on a phosphoric acid basis in order to improve stacking whitening resistance and filament
20 tape resistance and to obtain a dry coating film 3 in which the first component 31 and the second component 32 are arranged more uniformly. When the P content in the dry coating film 3 is less than or equal to 7.5 mass% and preferably less than or equal to 7.0 mass% on a phosphoric acid basis, good blackening resistance is obtained, and the contained amounts of the other components can be ensured sufficiently and
25 therefore more excellent corrosion resistance is obtained.

[0050]

Titanium (Ti) and vanadium (V) are components having corrosion suppression action, and improve the corrosion resistance of the surface-treated steel sheet 10. Ti and V are different in the corrosion environment in which a function as
30 a corrosion inhibitor is exhibited effectively. Thus, by the containing of two kinds of elements of Ti and V as corrosion inhibitors, corrosion in various corrosion

environments can be suppressed by the synergy of Ti and V, and more excellent corrosion resistance is obtained.

[0051]

The Ti content in the dry coating film 3 is preferably 1.7 to 2.4 mass%.
5 When the Ti content is more than or equal to 1.7 mass% and more preferably more than or equal to 1.9 mass%, a dry coating film 3 in which the effect of improving corrosion resistance by containing Ti is obtained sufficiently is obtained, and a surface-treated steel sheet 10 more excellent in corrosion resistance is obtained. When the Ti content is less than or equal to 2.4 mass% and more preferably less than
10 or equal to 2.3 mass%, the contained amounts of the other components can be ensured sufficiently, and therefore more excellent corrosion resistance is obtained.

[0052]

The V content in the dry coating film 3 is preferably 0.70 to 0.90 mass%.
When the V content is more than or equal to 0.70 mass% and more preferably more
15 than or equal to 0.75 mass%, a dry coating film 3 in which the effect of improving corrosion resistance based on vanadium is obtained sufficiently is obtained, and a surface-treated steel sheet 10 more excellent in corrosion resistance is obtained. When the V content is less than or equal to 0.90 mass%, the contained amounts of the other components can be ensured sufficiently, and therefore more excellent
20 corrosion resistance is obtained.

[0053]

The mass ratio between Ti and V (Ti/V) in the dry coating film 3 is preferably 2.1 to 2.9. When (Ti/V) is more than or equal to 2.1 and more preferably more than or equal to 2.2, a dry coating film 3 in which the effect of improving
25 corrosion resistance based on titanium is obtained sufficiently is obtained, and a surface-treated steel sheet 10 having excellent processability is obtained. When (Ti/V) is less than or equal to 2.9 and more preferably less than or equal to 2.8, the effect of improving corrosion resistance based on vanadium is obtained sufficiently, and therefore more excellent corrosion resistance is obtained.

30 [0054]

Silicon (Si) has film production action and exhibits barrier properties and

adhesiveness, and thereby improves corrosion resistance, water condensation whitening resistance, and stacking whitening resistance.

The Si content in the dry coating film 3 is preferably 10 to 40 mass% on a SiO₂ basis. A dry coating film 3 in which the Si content in the dry coating film 3 is more than or equal to 10 mass% and preferably more than or equal to 20 mass% on a SiO₂ basis is formed using a water-based surface treatment agent containing Si sufficiently. Therefore, by applying and drying the water-based surface treatment agent, a dry coating film 3 excellent in barrier properties in which three-dimensional crosslinks based on siloxane bonds are formed is obtained. As a result, a dry coating film 3 having even more excellent effect of improving corrosion resistance is obtained. When the Si content in the dry coating film 3 is less than or equal to 40 mass% and preferably less than or equal to 30 mass% on a SiO₂ basis, the contained amounts of the other components can be ensured sufficiently, and therefore more excellent corrosion resistance is obtained.

[0055]

The contained amounts of P, Ti, V, and Si in the dry coating film 3 can be calculated by performing X-ray fluorescence analysis on the dry coating film 3, while regarding P, Ti, V, and Si in the dry coating film 3 as existing as oxides. A study by the present inventors has shown that the components of P (on a phosphoric acid basis), Ti, V, and Si (on a SiO₂ basis) in the dry coating film calculated by the method mentioned above correspond to the mass ratios (phosphoric acid, Ti, V, and Si (on a SiO₂ basis)) to the total solid content of the water-based surface treatment agent. Thus, the contained amounts (mass%) of P (on a phosphoric acid basis), Ti, V, and Si (on a SiO₂ basis) in the dry coating film 3 can be regarded as the mass ratios in percentage to the total solid content of the water-based surface treatment agent.

[0056]

The dry coating film 3 may contain fluoride ions. Fluoride ions in the dry coating film 3 are derived from, for example, a component containing fluoride ions that is contained in the water-based surface treatment agent used when forming the dry coating film 3, as necessary. The component containing fluoride ions may be

used in order for the components that constitute the dry coating film 3 to be water-solubilized or solubilized in the water-based surface treatment agent. The contained amount of fluoride ions in the dry coating film 3 is not particularly limited; for example, when the amount is less than $0.3 \text{ mg}\cdot\text{m}^{-2}$, the occurrence of water
5 condensation whitening due to containing fluoride ions can be prevented more reliably. In more detail, when the contained amount of fluoride ions is less than $0.3 \text{ mg}\cdot\text{m}^{-2}$, the amount of fluoride ions dissolved out into condensation water is small. Thus, even when fluoride ions are concentrated and precipitated on the dry coating film 3 in the step of removing condensation water to dryness, the amount of fluoride
10 ions is limited to such a very small amount that fluoride ions do not appear as water condensation whitening. Therefore, the worsening of the external appearance (the occurrence of white rust) due to water condensation whitening can be prevented.

[0057]

2. Method for producing surface-treated steel sheet

15 Next, a method for producing a surface-treated steel sheet of the present embodiment is described using an example.

First, the steel sheet 1 is prepared, and a plating layer 2 containing zinc is formed on one surface or both surfaces of the steel sheet 1 by a conventionally known method.

20 Next, the present embodiment describes a method in which the dry coating film 3 is formed on the plating layer 2 by applying, on the plating layer 2, a water-based surface treatment agent containing the components to be contained in the dry coating film 3 mentioned above at a prescribed ratio and drying the water-based surface treatment agent.

25 [0058]

2.1 Water-based surface treatment agent

In the present embodiment, for example, a water-based surface treatment agent containing a polyurethane resin (A), a phenolic resin (B), a silane coupling agent (C), an acetylacetone complex of titanium (D), a vanadium compound (E),
30 olefin-based wax (F), an acetic acid component (G), a phosphoric acid component (H), and water is used as the water-based surface treatment agent.

[0059]

<Polyurethane resin (A)>

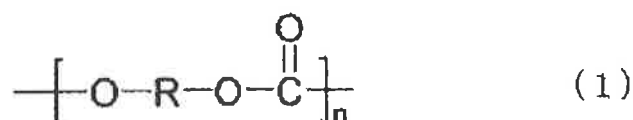
The polyurethane resin (A) contained in the water-based surface treatment agent exists as water-dispersible resin particles (dispersion) with an average particle size of 20 to 200 nm dispersed in water. The polyurethane resin (A) is preferably a cationic polyurethane resin. The cationic polyurethane resin is preferably one in which the surface of the resin particle is modified with an amine. The modification with an amine is preferably modification with a tertiary or lower amine. In the case of modification with a quaternary amine, water resistance is degraded by a plus charge existing in the dry coating film 3 formed by applying and drying the water-based surface treatment agent. The modification with an amine is preferably modification with a tertiary amine from the viewpoint of achieving both the dispersibility of resin particles in the dry coating film 3 and the water resistance of the dry coating film 3.

15 [0060]

The cationic polyurethane resin is preferably a polycarbonate-based cationic polyurethane resin containing a structural unit represented by General Formula (1) below. In the case where the cationic polyurethane resin contains a structural unit represented by General Formula (1) below, more excellent barrier properties are imparted to the dry coating film 3 formed by applying and drying the water-based surface treatment agent, and therefore corrosion resistance, water condensation whitening resistance, and stacking whitening resistance are improved.

[0061]

[Chem. 1]



25

[0062]

In General Formula (1) above, R represents an aliphatic alkylene group having 4 to 9 carbon atoms, and n represents an integer corresponding to the case where the number average molecular weight of a carbonate-based polyol that is a

source material of the polycarbonate-based cationic polyurethane resin mentioned above is in the range of 500 to 5000.

[0063]

<Phenolic resin (B)>

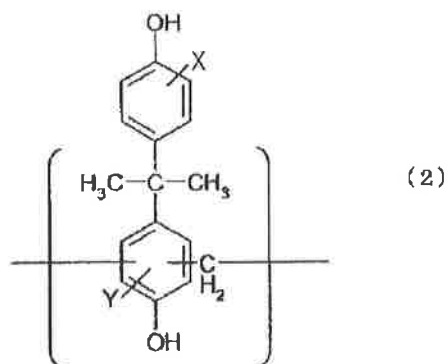
- 5 The phenolic resin (B) is contained in the water-based surface treatment agent as necessary, and may not be contained. When the phenolic resin (B) is contained in the water-based surface treatment agent, the stability of the water-based surface treatment agent is improved.

[0064]

- 10 The phenolic resin (B) is preferably a cationic phenolic resin (B). The cationic phenolic resin is preferably one having a repeating unit represented by General Formula (2) below. The cationic phenolic resin is more preferably a polymer molecule in which the average degree of polymerization of a repeating unit represented by General Formula (2) below is 2 to 50. When the average degree of polymerization is within the range mentioned above, a dry coating film 3 having excellent water resistance is obtained, and therefore more excellent corrosion resistance is obtained. The average degree of polymerization of a repeating unit of General Formula (2) can be found from an integration ratio by ¹H-NMR.

[0065]

- 20 [Chem. 2]



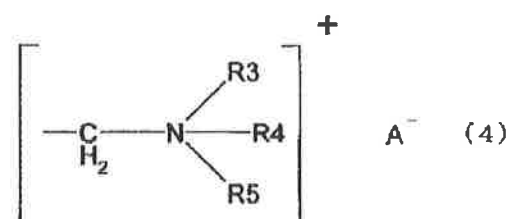
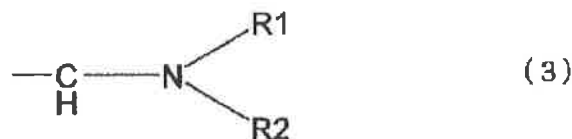
[0066]

In General Formula (2) above, X and Y independently represent hydrogen or a Z group represented by General Formula (3) or General Formula (4), and the

average number of substituents of Z groups per benzene ring is 0.2 to 1.0. The average number of substituents of Z groups can be found from an integration ratio by $^1\text{H-NMR}$.

[0067]

5 [Chem. 3]



[0068]

R1, R2, R3, R4, and R5 in General Formula (3) and General Formula (4) above independently represent a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, or a hydroxyalkyl group having 1 to 10 carbon atoms, and A⁻ represents a hydroxide ion or an oxoacid (for example, nitrate, sulfate, phosphate, carbonate, carboxylate, or the like) ion.

[0069]

For the water-based surface treatment agent, it is preferable that an anion that volatilizes during drying and film production be used as a counter-anion to each of the cationic polyurethane resin and the cationic phenolic resin. As the anion that volatilizes during drying and film production, specifically, a formate ion or an acetate ion is preferable.

[0070]

20 <Silane coupling agent (C)>

The silane coupling agent (C) is turned into a silanol by hydrolysis in the step of drying (baking) a wet coating film formed by applying the water-based surface treatment agent, and forms a siloxane-type dry coating film that is three-dimensionally crosslinked by siloxane bonds.

As the silane coupling agent (C), an alkoxysilane having 2 or more, preferably 3 or more alkoxy groups is preferably used. As the silane coupling agent (C), also a partially hydrolyzed product of the alkoxysilane mentioned above may be used.

5 [0071]

The alkoxy group of the silane coupling agent (C) hydrolyzes in the water-based surface treatment agent, and produces a silanol (-Si-OH). When the pH of the water-based surface treatment agent is less than or equal to 6.5, the dispersion stability of the silanol in the water-based surface treatment agent is good.

10 [0072]

Examples of the silane coupling agent (C) include N-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropylmethyldimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, vinyltriethoxysilane, 3-mercaptopropyltrimethoxysilane, 3-methacryloxypropyltrimethoxysilane, and the like.

[0073]

As the silane coupling agent (C), among the above, one having a functional group reactive with the polyurethane resin (A) and the phenolic resin (B) is preferably used. As such a silane coupling agent (C), for example, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane, 3-mercaptopropyltrimethoxysilane, and the like are preferable, and 3-aminopropyltriethoxysilane and 3-glycidoxypropyltrimethoxysilane are particularly preferable.

25 The kind of the reaction between the polyurethane resin (A) and the phenolic resin (B), and the silane coupling agent (C) may be polymerization reaction, condensation reaction, addition reaction, or the like, and is not particularly limited.

[0074]

<Acetylacetone complex of titanium (D)>

30 The acetylacetone complex of titanium (D) in the water-based surface treatment agent reacts with the plating layer 2 in the step of drying (baking) a wet

coating film formed by applying the water-based surface treatment agent, and is precipitated as a titanium compound in the dry coating film 3. Even when an acetylacetonate and acetylacetone derived from the acetylacetone complex of titanium (D) exist in the dry coating film 3, these have weak ionicity, and therefore do not adversely influence the likelihood of water condensation whitening. Examples of the acetylacetone complex of titanium (D) include titanium diisopropoxy bis(acetylacetonate), titanium tetrakis(acetylacetonate), and the like.

[0075]

<Vanadium compound (E)>

As the vanadium compound (E), a compound not containing a strong electrolyte or a salt with a volatile acid is preferably used. As the vanadium compound (E) not containing a strong electrolyte, vanadium pentoxide, metavanadic acid and a salt thereof (for example, ammonium metavanadate), vanadium trioxide, vanadium dioxide, vanadium oxyacetylacetonate, vanadium acetylacetonate, or the like is given. As the salt with a volatile acid, vanadium acetate or the like is given. Among the vanadium compounds (E) mentioned above, an acetylacetone complex of vanadium such as vanadium acetylacetonate or vanadium oxyacetylacetonate is used particularly preferably in view of the effect of improving corrosion resistance.

[0076]

<Olefin-based wax (F)>

The olefin-based wax (F) is contained in the water-based surface treatment agent as necessary, and may not be contained. The olefin-based wax (F) is preferably contained in the water-based surface treatment agent in order to impart lubricity to the dry coating film 3.

Examples of the olefin-based wax (F) include polyethylene wax, polyethylene oxide wax, polypropylene oxide wax, and the like.

[0077]

The resin particle made of the olefin-based wax (F) is preferably surface-modified with a silane coupling agent (I). In the case where the olefin-based wax (F) is one surface-modified with the silane coupling agent (I), the wettability of the olefin-based wax (F) in the water-based surface treatment agent is increased. Thus,

the dry coating film 3 obtained by applying and drying the water-based surface treatment agent is made to be a dry coating film in which resin particles made of the olefin-based wax (F) are dispersed even more uniformly.

[0078]

5 As the silane coupling agent (I) used for the surface modification of the olefin-based wax (F), a silane coupling agent having a reactive functional group is preferably used. The olefin-based wax (F) surface-modified with the silane coupling agent (I) is preferably one in which a polyethylene wax emulsion having a carboxyl group is surface-modified with a silane coupling agent containing an epoxy
10 group (for example, 3-glycidoxypropyltrimethoxysilane).

[0079]

 The ratio (I/F) of the mass of the silane coupling agent (I) to the mass of the olefin-based wax (F) is preferably 0.025 to 0.035. The added amount of the silane coupling agent (I) is preferably more than or equal to, in moles, the acid value of a
15 dispersion of the olefin-based wax (F) used for the water-based surface treatment agent.

[0080]

<Acetic acid component (G)>

 The acetic acid component (G) improves the stability of the water-based
20 surface treatment agent. It is surmised that this effect is due to the fact that the pH of the water-based surface treatment agent is stabilized at 3.5 to 4.0 by the pH buffer action of the acetic acid component (G), and thus the dispersion stability of the silane coupling agent (C) that has been turned into a silanol is enhanced and the condensation reaction of the silane coupling agent (C) is slowed. A study by the
25 present inventors has shown that the pH at which the condensation reaction of the silane coupling agent (C) is slowest is 3.5 to 4.0.

[0081]

 The acetic acid component (G) enhances the dispersion stability of the silane coupling agent (C) as described above, and accordingly suppresses the
30 aggregation and association of resin particles of the first component. In contrast, in the case where the water-based surface treatment agent does not contain the acetic

acid component (G), each component of such a water-based surface treatment agent is not stabilized, and consequently the first component cannot disperse uniformly or finely in the formed dry coating film.

[0082]

5 Examples of the acetic acid component (G) include acetic acid, ammonium acetate, potassium acetate, sodium acetate, and the like. Acetic acid is particularly preferable in view of the chemical agent stability of the water-based surface treatment agent. Further, the boiling point of acetic acid is 118°C, which is a lower boiling point among the boiling points of organic acids having buffer action, and
10 acetic acid is less likely to remain in the dry coating film 3. Thus, acetic acid is suitable as the acetic acid component (G) that is put in the water-based surface treatment agent.

[0083]

<Phosphoric acid component (H)>

15 Examples of the phosphoric acid component (H) include inorganic phosphate compounds such as phosphoric acid, ammonium phosphate, potassium phosphate, sodium phosphate, and monosodium dihydrogen phosphate. Among these, in particular, phosphoric acid is preferably used as the phosphoric acid component (H) in view of the effect of improving stacking whitening resistance and
20 filament tape resistance and an effect in which a dry coating film 3 in which the first component 31 and the second component 32 are arranged more uniformly is obtained.

[0084]

 The phosphoric acid component (H) contained in the water-based surface treatment agent reacts with the plating layer 2, and produces a zinc phosphate dry
25 coating film on the surface of the plating layer 2. The zinc phosphate dry coating film suppresses the dissolving-out of zinc from the plating layer 2, and suppresses the occurrence of white rust. Further, the phosphoric acid component (H) reduces the amount of the acetic acid component (G) remaining in the dry coating film 3. As a result, an event in which an adhesive layer of a tape of FIRMEN-TEPU that is
30 used to temporarily stick an end portion of a coil formed of the surface-treated steel sheet 10 is attacked by the acetic acid component (G) can be prevented, and the

adhesiveness reduction of the tape of FIRAMEN-TEPU can be suppressed. Further, a reduction in water condensation whitening resistance due to the acetic acid component (G) remaining in the dry coating film 3 can be prevented.

[0085]

- 5 As the phosphoric acid component (H), an inorganic phosphate is preferable in view of stability in a chemical agent.

[0086]

Preferred blending ratios of the components contained in the water-based surface treatment agent used in the present embodiment are as follows.

- 10 (1) The ratio (NC)/(NV) of the mass of the silane coupling agent (C) on a SiO₂ basis to the mass of the solid content (V) of the water-based surface treatment agent is 0.10 to 0.40

(2) The ratio (ND)/(NV) of the mass (ND) of the acetylacetone complex of titanium (D) on a Ti basis to the mass of the solid content (V) is 0.017 to 0.024

- 15 (3) The ratio (NE)/(NV) of the mass (NE) of the vanadium compound (E) on a V basis to the mass of the solid content (V) is 0.007 to 0.009

(4) The ratio (NF)/(NV) of the mass of the olefin-based wax (F) to the mass of the solid content (V) is 0.035 to 0.060

- 20 (5) The ratio (NG)/(NV) of the mass of the acetic acid component (G) to the mass of the solid content (V) is 0.04 to 0.14

(6) The ratio (NH)/(NV) of the mass of the phosphoric acid component (H) to the mass of the solid content (V) is 0.025 to 0.075

(7) The ratio (ND)/(NE) of the mass of the acetylacetone complex of titanium (D) on a Ti basis to the mass of the vanadium compound (E) on a V basis is 2.1 to 2.9

- 25 (8) The ratio (NH)/(NG) of the mass of the phosphoric acid component (H) to the mass of the acetic acid component (G) is 0.25 to 1.1

[0087]

<(NC)/(NV)>

- 30 The ratio (NC)/(NV) of the mass of the silane coupling agent (C) on a SiO₂ basis to the mass of the solid content (V) of the water-based surface treatment agent is preferably 0.10 to 0.40, and more preferably 0.16 to 0.19. When (NC)/(NV) is

less than or equal to 0.40, the contained amounts of the other components can be ensured sufficiently, and therefore the effect of improving corrosion resistance based on other components is obtained sufficiently. When (NC)/(NV) is more than or equal to 0.10, three-dimensional crosslinks based on siloxane bonds are formed sufficiently, and a dry coating film 3 having excellent corrosion resistance, water condensation whitening resistance, and stacking whitening resistance is obtained.

[0088]

<(ND)/(NV)>

The ratio (ND)/(NV) of the mass (ND) of the acetylacetone complex of titanium (D) on a Ti basis to the mass of the solid content (V) mentioned above is 0.017 to 0.024, and preferably 0.019 to 0.023. When (ND)/(NV) is more than or equal to 0.017, a dry coating film 3 in which the effect of improving corrosion resistance based on the titanium compound (D) is obtained sufficiently is obtained. When (ND)/(NV) is less than or equal to 0.024, the contained amounts of the other components can be ensured sufficiently, and therefore the effect of improving corrosion resistance based on other components is obtained sufficiently.

[0089]

<(NE)/(NV)>

The ratio (NE)/(NV) of the mass (NE) of the vanadium compound (E) on a V basis to the mass of the solid content (V) mentioned above is 0.0070 to 0.0090, and preferably 0.0075 to 0.0090. When (NE)/(NV) is more than or equal to 0.0070, a dry coating film 3 in which the effect of improving corrosion resistance based on the vanadium compound (E) is obtained sufficiently is obtained. When (NE)/(NV) is less than or equal to 0.0090, the contained amounts of the other components can be ensured sufficiently, and therefore the effect of improving corrosion resistance based on other components is obtained sufficiently.

[0090]

<(NF)/(NV)>

The ratio (NF)/(NV) of the mass of the olefin-based wax (F) to the mass of the solid content (V) mentioned above is 0.035 to 0.060, and preferably 0.040 to 0.055. When (NF)/(NV) is more than or equal to 0.035, a dry coating film 3 having

sufficient lubricity is obtained, and a surface-treated steel sheet 10 with good processability is obtained. When $(NF)/(NV)$ is less than or equal to 0.060, a surface-treated steel sheet 10 with good handleability is obtained.

[0091]

5 $<(NG)/(NV)>$

The ratio $(NG)/(NV)$ of the mass of the acetic acid component (G) to the mass of the solid content (V) mentioned above is 0.04 to 0.14, preferably 0.05 to 0.13, and more preferably 0.06 to 0.12. When $(NG)/(NV)$ is more than or equal to 0.04, the stability of the water-based surface treatment agent is even better. When
10 $(NG)/(NV)$ is less than or equal to 0.14, a reduction in water condensation whitening resistance due to the remaining of the acetic acid component (G) in the dry coating film 3 can be prevented.

[0092]

$<(NH)/(NV)>$

15 The ratio $(NH)/(NV)$ of the mass of the phosphoric acid component (H) to the mass of the solid content (V) mentioned above is 0.025 to 0.075, preferably 0.030 to 0.070, and more preferably 0.035 to 0.065. Since $(NH)/(NV)$ is more than or equal to 0.025, the dissolving-out of zinc from the plating layer 2 can be suppressed. Further, at the stage when the water-based surface treatment agent is applied on the
20 plating layer 2, the phosphoric acid component (H) in the water-based surface treatment agent is deposited on the surface of the plating layer 2, and the surface energy of the plating layer 2 becomes appropriate; thus, a wet coating film in which the first component 31 is dispersed substantially uniformly in a self-aligned manner is formed. When $(NH)/(NV)$ is less than or equal to 0.075, the contained amounts
25 of the other components can be ensured sufficiently, and therefore the effect of improving corrosion resistance based on other components is obtained sufficiently.

[0093]

$<(ND)/(NE)>$

30 The ratio $(ND)/(NE)$ of the mass of the acetylacetone complex of titanium (D) on a Ti basis to the mass of the vanadium compound (E) on a V basis is 2.1 to 2.9, preferably 2.2 to 2.8, and more preferably 2.3 to 2.7. When $(ND)/(NE)$ is more than

or equal to 2.1, a dry coating film 3 in which the effect of improving corrosion resistance based on the titanium compound (D) is obtained sufficiently is obtained. When (ND)/(NE) is less than or equal to 2.9, a dry coating film 3 in which the effect of improving corrosion resistance based on the vanadium compound (E) is obtained sufficiently is obtained. When (ND)/(NE) is 2.1 to 2.9, corrosion in various corrosion environments can be suppressed by the synergy of Ti and V, and a dry coating film 3 having more excellent corrosion resistance is obtained.

[0094]

<(NH)/(NG)>

10 The ratio (NH)/(NG) of the mass of the phosphoric acid component (H) to the mass of the acetic acid component (G) is 0.25 to 1.1, preferably 0.30 to 1.0, and more preferably 0.35 to 0.9. When (NH)/(NG) is 0.25 to 1.1, the effect of improving the stability of the water-based surface treatment agent based on the acetic acid component (G) is obtained sufficiently, and the reduction in water condensation whitening resistance and the reduction in the adhesiveness of a tape of FIRAMEN-TEPU due to the remaining of the acetic acid component (G) in the dry coating film 3 can be suppressed.

[0095]

20 The water-based surface treatment agent can be prepared by dissolving or dispersing the components mentioned above in a water-based solvent at the blending ratios mentioned above. Each component is adjusted to a prescribed ratio to the mass of the nonvolatile content (the solid content (V)) excluding the solvent and the volatile components (the mass of the dry coating film) so as to be at a prescribed ratio in the dry coating film 3.

25 The water-based solvent used for the water-based surface treatment agent may be water alone. For the purpose of improving the dryability of a wet coating film formed by applying the water-based surface treatment agent, etc., a water-soluble organic solvent not containing a strong electrolyte (for example, alcohols) may be put in the water-based solvent used for the water-based surface treatment agent in a contained amount of, for example, less than or equal to 30 mass% of the entire water-based solvent.

[0096]

<pH>

The pH of the water-based surface treatment agent is preferably 2.0 to 6.5. When the pH of the water-based surface treatment agent is less than or equal to 6.5, the dispersion stability of the silane coupling agent (C) is good. When the pH of the water-based surface treatment agent is more than or equal to 2.0, the handling of the water-based surface treatment agent is easy, and damage to facilities by the water-based surface treatment agent can be prevented; thus, this is preferable. The pH of the water-based surface treatment agent can be adjusted by, for example, adding a volatile acid such as acetic acid or formic acid to the water-based surface treatment agent.

[0097]

<Component containing fluoride ions>

A component containing fluoride ions may be contained in the water-based surface treatment agent, as necessary. The component containing fluoride ions is used so that the components that constitute the dry coating film 3 are water-solubilized or solubilized in the water-based surface treatment agent.

Examples of the component containing fluoride ions contained in the water-based surface treatment agent include sodium fluoride, potassium fluoride, calcium fluoride, lithium fluoride, titanium hydrofluoric acid, zirconium hydrofluoric acid, and the like.

[0098]

An additive commonly used for a treatment liquid for application, such as a leveling agent or an antifoaming agent, may be added to the water-based surface treatment agent.

[0099]

2.2 Method for forming a dry coating film

In the present embodiment, the water-based surface treatment agent thus obtained is applied on the plating layer 2, and thereby a wet coating film is formed. As a method for applying the water-based surface treatment agent on the plating layer 2, a roll coater is preferably used. In the case of application using a roll coater,

the film thickness can be controlled easily by adjusting the peripheral speed ratio, and excellent productivity is obtained.

[0100]

In the present embodiment, holding is performed for 0.1 to 10 seconds from
5 the time when the water-based surface treatment agent is applied on the plating layer and a wet coating film is formed to the time when drying is started. By performing holding in the state of a wet coating film for more than or equal to 0.1 seconds and more preferably more than or equal to 0.2 seconds, the first component 31 in the wet coating film disperses substantially uniformly and stably in a self-aligned manner.
10 Even if the time from when a wet coating film is formed to when drying is started is set to more than 10 seconds, the effect of the first component 31 in the wet coating film dispersing uniformly is not improved, and productivity is reduced. If the time from when a wet coating film is formed to the start is a long time, aggregation and local existence of particles of the first component 31 tend to occur. Thus, the time
15 of holding in the state of a wet coating film is preferably less than or equal to 10 seconds, and more preferably less than or equal to 5 seconds.

[0101]

Next, the wet coating film held for a prescribed time is dried. The temperature at the time of drying the wet coating film is selected to be a temperature
20 at which the counter-anions to the cationic polyurethane resin and the cationic phenolic resin and the acetic acid component (G), which are volatile components in the water-based surface treatment agent, volatilize. Specifically, it is preferable that the peak metal temperature (PMT) at the time of drying the wet coating film be within the range of 60 to 150°C. Examples of the drying method for drying the wet
25 coating film include hot-air drying, induction heating, and in-furnace drying.

[0102]

When the volatile components in the wet coating film are volatilized by drying the wet coating film, the pH in the wet coating film rises. Thereby, the plating layer 2, the acetylacetone complex of titanium (D), the silane coupling agent
30 (C) that has been turned into a silanol by hydrolysis, the cationic polyurethane resin, and the cationic phenolic resin react while the state where the first component 31 is

dispersed substantially uniformly is maintained. As a result, the surface of the plating layer 2, and the polyurethane resin, the phenolic resin, the siloxane compound, and the titanium compound form a strong network based on ionomer bonds, metaloxane bonds, or siloxane bonds, and the vanadium compound and the olefin-based wax are fixed to the network; thus, a dry coating film 3 in which the first component 31 and the second component 32 are dispersed substantially uniformly is formed.

By the above steps, a surface-treated steel sheet of the present embodiment is obtained.

10 [0103]

Although the present embodiment is described using, as an example, a case where a water-based surface treatment agent containing the phenolic resin (B) and the olefin-based wax (F) is used when forming the dry coating film 3, the dry coating film 3 may be formed using a water-based surface treatment agent not containing the phenolic resin (B) and/or the olefin-based wax (F).

[Examples]

[0104]

Next, Examples of the present invention are described. Note that the present invention is not limited to Examples shown below.

20 [0105]

1. Production of surface-treated steel sheet

Water-based surface treatment agents X1 to X46 containing the components shown in Table 1 and below in the contained amounts shown in Table 2 were prepared. The solid content in the water-based surface treatment agent was adjusted to 11 mass%.

[0106]

(Components of water-based surface treatment agent)

[Polyurethane resin (A)]

A1: Polyurethane resin (average particle size: 60 nm)

30 A2: Polyurethane resin (average particle size: 10 nm)

A3: Polyurethane resin (average particle size: 300 nm)

[0107]

[Phenolic resin (B)]

B1: Cationic phenolic resin

The average degree of polymerization n of a repeating unit of General Formula (2) =

5 5

X of General Formula (2) = $-\text{CH}_2\text{N}(\text{CH}_3)_2$

Y of General Formula (2) = H

The degree of Z-substitution of General Formula (2) = 0.5

[0108]

10 [Silane coupling agent (C)]

C1: 3-Aminopropyltriethoxysilane

C2: 3-Glycidoxypropyltrimethoxysilane

C3: 3-Mercaptopropyltrimethoxysilane

[0109]

15 [Acetylacetone complex of titanium (D)]

D1: Titanium diisopropoxy bis(acetylacetonate)

D2: Titanium tetrakis(acetylacetonate)

D3: Titanium hydrofluoric acid (a component containing fluoride ions)

[Vanadium compound (E)]

20 E1: Vanadium acetylacetonate

[0110]

[Olefin-based wax (F)]

F1: Olefin-based wax with an average particle size of $0.05\ \mu\text{m}$

25 F2: Olefin-based wax with an average particle size of $0.05\ \mu\text{m}$, surface-modified with a silane coupling agent (3-glycidoxypropyltrimethoxysilane). The contained amount of the silane coupling agent contained in the olefin-based wax [mass of silane coupling agent/mass of olefin-based wax] = 0.030

[0111]

[Acetic acid component (G)]

30 G1: Acetic acid

[Phosphoric acid component (H)]

H1: Phosphoric acid

[0112]

[Table 1]

[0113]

[Table 2]

Agent No.	Contained amount (solid content mass ratio; ratio to total solid content)										Fluorine (mg·m ⁻²)	D/E
	Resin		(C), on SiO ₂ basis			(D), on Ti basis	(E), on V basis	Wax	Acetic acid	Phosphoric acid		
	(A)	(B)	(C1)	(C2)	Total C	(D)	(E)	(F)	(G)	(H)		
X1	0.32	0.03	0.11	0.05	0.16	0.022	0.0085	0.05	0.07	0.040	-	2.6
X2	0.32	0.03	0.12	0.07	0.19	0.021	0.0085	0.05	0.11	0.060	-	2.5
X3	0.32	0.03	0.12	0.06	0.18	0.017	0.0075	0.05	0.08	0.050	-	2.3
X4	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X5	0.32	0.03	0.12	0.06	0.18	0.024	0.0085	0.05	0.08	0.050	-	2.8
X6	0.32	0.03	0.12	0.06	0.18	0.019	0.0070	0.05	0.08	0.050	-	2.7
X7	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.07	0.060	-	2.6
X8	0.32	0.03	0.12	0.06	0.18	0.022	0.0090	0.05	0.08	0.050	-	2.4
X9	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0	0.07	0.060	-	2.6
X10	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.04	0.027	-	2.6
X11	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.05	0.027	-	2.5
X12	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.13	0.055	-	2.5
X13	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.14	0.055	-	2.6
X14	0.32	0.03	0.12	0.06	0.18	0.019	0.0075	0.05	0.07	0.025	-	2.5
X15	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.07	0.030	-	2.5
X16	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.070	-	2.5
X17	0.32	0.03	0.12	0.06	0.18	0.023	0.0085	0.05	0.11	0.075	-	2.7
X18	0.35	0	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X19	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.07	0.060	-	2.6
X20	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X21	0.32	0.03	0.18	0	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X22	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X23	0.32	0.03	0.11	0.05	0.15	0.022	0.0085	0.05	0.07	0.060	-	2.6
X24	0.32	0.03	0.12	0.07	0.20	0.021	0.0085	0.05	0.11	0.040	-	2.5
X25	0.32	0.03	0.12	0.06	0.18	0.016	0.0073	0.05	0.08	0.050	-	2.2
X26	0.32	0.03	0.12	0.06	0.18	0.025	0.0088	0.05	0.08	0.050	-	2.8
X27	0.32	0.03	0.12	0.06	0.18	0.017	0.0060	0.05	0.08	0.050	-	2.8
X28	0.32	0.03	0.12	0.06	0.18	0.022	0.0100	0.05	0.08	0.050	-	2.2
X29	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.03	0.030	-	2.6
X30	0.32	0.03	0.12	0.06	0.18	0.022	0.0085	0.05	0.15	0.070	-	2.6
X31	0.32	0.03	0.12	0.06	0.18	0.017	0.0075	0.05	0.08	0.050	0.2	2.3
X32	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5
X33	0.32	0.03	0.12	0.06	0.18	0.021	0.0085	0.05	0.11	0.040	-	2.5

[0114]

Steel sheets shown below each having plating layers on both surfaces and having the surface roughness (Ra-S) shown in Table 3 and Table 4 were prepared. Each steel sheet having plating layers on both surfaces has a plating layer with a zinc
 5 content of more than or equal to 40 mass%. The surface roughness (Ra-S) of the steel sheet shown in Table 3 and Table 4 was found by forming a dry coating film by a method described later to obtain a surface-treated steel sheet, and using a contact roughness meter to measure the surface roughness (Ra) of a measurement length of 1 inch in an arbitrary place of the surface of the dry coating film of the surface-treated
 10 steel sheet.

[0115]

(Steel sheet having plating layers on both surfaces)

- EG

NS JIN-KOTO (registered trademark), manufactured by Nippon Steel & Sumitomo
 15 Metal Corporation, a zinc-electroplated steel sheet, the sheet thickness: 0.8 mm, the attached amount of plating of one surface: 20 g/m²

- GI

NS SHIRUBA-JINKU (registered trademark), manufactured by Nippon Steel & Sumitomo Metal Corporation, a zinc-hot-dipped steel sheet, the sheet thickness: 0.8
 20 mm, the attached amount of plating of one surface: 60 g/m²

- GI(Sb)

NS SHIRUBA-JINKU (registered trademark), manufactured by Nippon Steel & Sumitomo Metal Corporation, an antimony-containing zinc-hot-dipped steel sheet, the sheet thickness: 0.8 mm, the attached amount of plating of one surface: 60 g/m²

25 [0116]

- GA

NS SHIRUBA-AROI (registered trademark), manufactured by Nippon Steel & Sumitomo Metal Corporation, an alloyed zinc-hot-dipped steel sheet, the sheet thickness: 0.8 mm, the attached amount of plating of one surface: 60 g/m²

30 - SD

SUPA-DAIMA (registered trademark), manufactured by Nippon Steel & Sumitomo

Metal Corporation, a zinc-aluminum-magnesium-silicon alloy-plated steel sheet, the sheet thickness: 0.8 mm, the attached amount of plating of one surface: 60 g/m²

- ZL

- NS JINKU-RAITO (registered trademark), manufactured by Nippon Steel & Sumitomo Metal Corporation, a zinc-nickel alloy-plated steel sheet, the sheet thickness: 0.8 mm, the attached amount of plating of one surface: 20 g/m², the nickel content in the plating layer: 12 mass%
- 5

[0117]

[Table 3]

No.	Agent	Steel sheet	Ra-S					Drying conditions		Interference pattern (9)
			Roughness of surface of steel sheet (Ra, μm)					Wet coating film holding time (seconds)	PMT (°C)	
			Less than 0.1	More than or equal to 0.1 and less than 0.2	More than or equal to 0.2 and less than 1.5	More than or equal to 1.5 and less than or equal to 2.0	More than 2.0			
Example 1	X1	GI			✓			2	80	A
Example 2	X2	GI			✓			2	80	A
Example 3	X3	GI			✓			2	80	A
Example 4	X4	GI			✓			2	80	A
Example 5	X5	GI			✓			2	80	A
Example 6	X6	GI			✓			2	80	A
Example 7	X7	GI			✓			2	80	A
Example 8	X8	GI			✓			2	80	A
Example 9	X9	GI			✓			2	80	A
Example 10	X10	GI			✓			2	80	A
Example 11	X11	GI			✓			2	80	A
Example 12	X12	GI			✓			2	80	A
Example 13	X13	GI			✓			2	80	A
Example 14	X14	GI			✓			2	80	A
Example 15	X15	GI			✓			2	80	A
Example 16	X16	GI			✓			2	80	A
Example 17	X17	GI			✓			2	80	A
Example 18	X18	GI			✓			2	80	A
Example 19	X19	GI			✓			2	80	A
Example 20	X20	GI			✓			2	80	A
Example 21	X21	GI			✓			2	80	A
Example 22	X22	GI			✓			2	80	A
Example 23	X23	GI			✓			2	80	A
Example 24	X24	GI			✓			2	80	A
Example 25	X25	GI			✓			2	80	A
Example 26	X26	GI			✓			2	80	A
Example 27	X27	GI			✓			2	80	A
Example 28	X28	GI			✓			2	80	A
Example 29	X29	GI			✓			2	80	A
Example 30	X30	GI			✓			2	80	A

[0118]

[Table 4]

No.	Agent	Steel sheet	Ra-S					Drying conditions		Interference pattern (9)
			Roughness of surface of steel sheet (Ra, μm)					Wet coating film holding time (seconds)	PMT (°C)	
			Less than 0.1	More than or equal to 0.1 and less than 0.2	More than or equal to 0.2 and less than 1.5	More than or equal to 1.5 and less than or equal to 2.0	More than 2.0			
Example 31	X4	GI			✓			2	60	A
Example 32	X4	GI			✓			2	150	A
Example 33	X4	GI		✓				2	80	B
Example 34	X4	GI				✓		2	80	A
Example 35	X4	GI(Sb)			✓			2	80	A
Example 36	X4	GA			✓			2	80	A
Example 37	X4	EG			✓			2	80	A
Example 38	X4	ZL			✓			2	80	A
Example 39	X4	SD			✓			2	80	A
Example 40	X31	GI			✓			2	80	A
Example 41	X4	GI(Sb)			✓			0.1	80	A
Example 42	X4	GI(Sb)			✓			0.2	80	A
Example 43	X4	GI(Sb)			✓			5	80	A
Example 44	X4	GI(Sb)			✓			10	80	A
Example 45	X4	GI(Sb)			✓			15	80	A
Example 46	X4	GI	✓					2	80	C
Example 47	X4	GI					✓	2	80	C
Comparative Example 1	X32	GI			✓			2	80	A
Comparative Example 2	X33	GI			✓			2	80	A
Comparative Example 3	X34	GI			✓			2	80	A
Comparative Example 4	X35	GI			✓			2	80	A
Comparative Example 5	X36	GI			✓			2	80	A
Comparative Example 6	X37	GI			✓			2	80	A
Comparative Example 7	X38	GI			✓			2	80	A
Comparative Example 8	X39	GI			✓			2	80	A
Comparative Example 9	X40	GI			✓			2	80	A
Comparative Example 10	X41	GI			✓			2	80	A
Comparative Example 11	X42	GI			✓			2	80	A
Comparative Example 12	X43	GI			✓			2	80	A
Comparative Example 13	X44	GI			✓			2	80	A
Comparative Example 14	X45	GI			✓			2	80	A
Comparative Example 15	X46	GI			✓			2	80	A

[0119]

Immediately after the formation of the plating layers, water-based surface treatment agents X1 to X46 shown in Table 2 were applied using a roll coater to both surfaces of the respective steel sheets having plating layers shown in Table 3 and Table 4. The peripheral speed ratio of the roll coater was adjusted so that the attached amount (weight after formation) of the dry coating film might be 700 (mg/m²) and the film thickness of the dry coating film might be 150 to 900 nm. The thickness of the dry coating film was found by observing a cross section of the surface-treated steel sheet using a TEM or a SEM, measuring the film thicknesses of the dry coating film in arbitrary five places, and calculating the average value. Holding was performed in the state of a wet coating film for the time (wet coating film holding time) shown in Table 3 and Table 4 from the time of the application to the time of the start of drying. The wet coating film holding time was adjusted by controlling the speed of transfer of the steel sheet from the roll coater to a heating furnace. The drying of the wet coating film was performed at the peak metal temperature (PMT) shown in Table 3 and Table 4 using an induction heating furnace. In Comparative Example 15, the formation of a dry coating film was not performed.

By the above steps, surface-treated steel sheets of Examples and Comparative Examples were obtained.

[0120]

2. Evaluation

For the surface-treated steel sheets of Examples and Comparative Examples thus obtained, the following items were evaluated by the following methods.

[0121]

2.1 Evaluation of dry coating film condition

(Average particle size of resin particle made of polyurethane resin in dry coating film)

For Example 4, Comparative Example 1, and Comparative Example 2, the average particle size of the resin particle made of a polyurethane resin in the dry coating film was measured using the method of observing the cross section of the dry coating film described above. The result was substantially equal to the average particle size of the polyurethane resin used as a material of the water-based surface

treatment agent (Example 4: 60 nm, Comparative Example 1: 10 nm, Comparative Example 2: 200 nm). Therefore, also the average particle size of the polyurethane resin of each of Examples 1 to 3, Examples 5 to 47, and Comparative Examples 3 to 15 was regarded as substantially equal to the average particle size of the polyurethane resin used as a material of the respective water-based surface treatment agent.

[0122]

(Contained amounts of P, Ti, V, and Si (on a SiO₂ basis) in dry coating film)

The contained amounts (mass%) of P (on a phosphoric acid basis), Ti, V, and Si (on a SiO₂ basis) in the dry coating film were regarded as the mass ratios in percentage to the total solid content of the water-based surface treatment agent shown in Table 2.

[0123]

(Contained amount of fluoride ions in dry coating film)

20 sets of 100 mm × 200 mm samples cut out from each surface-treated steel sheet were prepared. Next, each sample was immersed in 100 mL of water at 60°C for 10 minutes. Next, 2000 mL of the water in which the sample was immersed was collected and was concentrated by an evaporator, and the resulting substance was analyzed by ion chromatography. The result was used to calculate the contained amount (mg·m⁻²) of fluoride ions in the dry coating film. The results are shown in Table 2.

[0124]

(1) Area ratio of resin component in cross section of dry coating film

A carbon film was vapor-deposited as a protection film on a surface of the steel sheet, and a carbon film of several micrometers was formed using a focused ion beam processing apparatus (FIB), SMI3050SE, manufactured by Hitachi High-Tech Science Corporation. After that, a FIB was used to perform microsampling at an acceleration voltage of 30 kV (finish processing: 5 kV), and the sample was made into a thin film to obtain a sample of a cross section of the dry coating film. The obtained sample was observed using a TEM or a SEM having an energy dispersive X-ray spectroscope (EDS). For the dry coating film of each steel sheet, EDS

analysis (element mapping) of the cross sections of three places was performed, and maps of the elements of C, P, Ti, V, and Si were obtained. The obtained element map was divided into 100 squares (10×10) and was binarized into C and the other elements, and the area ratio of the resin component (C) in the cross section of the dry coating film was calculated; evaluation was performed in the following way.

1: Less than 35% or more than 80%

2: More than or equal to 35% and less than or equal to 80%

3: More than or equal to 40% and less than or equal to 60%

[0125]

Further, the dry coating film was peeled off from each steel sheet by acid treatment, and was subjected to infrared spectroscopic analysis and pyrolysis gas chromatography-mass spectrometry (GC-MS) analysis. Then, absorption derived from the resin component was observed in an infrared absorption spectrum of the dry coating film obtained by the infrared spectroscopic analysis, and analysis was performed using the belonging of the absorption; from the result of the analysis of infrared absorption and the result of the pyrolysis GC-MS, it was found that a urethane resin, a phenolic resin, and olefin-based wax were contained in the dry coating film.

Thus, results corresponding to the contained amounts in water-based surface treatment agents X1 to X46 shown in Table 2 were obtained.

[0126]

(2) Maximum value of distance between centers of gravity of resin particles

The maximum value of the distance between the centers of gravity of resin particles that were mutually adjacent and yet not mutually in contact (the distance between the centers in the case where the cross-sectional shape of each resin particle was regarded as a circular shape) was calculated in each of the cross sections of three places of each dry coating film that had been observed for the area ratio of the resin component in the cross section of the dry coating film by carbon element mapping of cross-sectional TEM-EDX; and the average value of the values obtained from the cross sections of three places was found, and was taken as the maximum value of the distance between the centers of gravity of resin particles. The obtained maximum

value of the distance between the centers of gravity of resin particles was evaluated in the following way using multiples of the average particle size. The specific gravity of the interior of the resin particle was regarded as fixed. The identification of the resin particle and the measurement of the average particle size and the center of gravity of the resin particle were performed by the method described above.

1: More than 3.0 times

2: More than 2.0 times and less than or equal to 3.0 times

3: Less than or equal to 2.0 times

[0127]

10 (3) Surface roughness (Ra-F) of dry coating film

The surface roughness (Ra) was measured using an atomic force microscope (AFM) in a $1\ \mu\text{m} \times 1\ \mu\text{m}$ measurement area in an arbitrary place of the surface of the dry coating film formed on the steel sheet having plating layers, and was evaluated in the following way.

15 1: More than 10 nm

2: More than or equal to 1 nm and less than or equal to 10 nm

[0128]

2.2 Evaluation of corrosion resistance

(4) Corrosion resistance

20 A corrosion resistance test was performed on each of an unprocessed test sheet (a flat surface portion), a test sheet that was crosscut with an NT cutter to the arrival at the base material (a crosscut portion), and a test sheet processed by Erichsen 7 mm extrusion (a processed portion). The evaluation method is as follows.

25 [0129]

(4)-1: Corrosion resistance of flat surface portion

The ratio of the white rust occurrence area as of 72 hours after salt water spraying was found and evaluated on the basis of the salt spray test method of JIS-Z-2371. The evaluation criteria are shown below (A to C are practical performance).

30 A: The ratio of the white rust occurrence area is less than 10%

B: The ratio of the white rust occurrence area is more than or equal to 10% and less

than 30%

C: The ratio of the white rust occurrence area is more than or equal to 30% and less than 60%

D: The ratio of the white rust occurrence area is more than or equal to 60%

5 [0130]

(4)-2: Corrosion resistance of crosscut portion

10 The situation of the occurrence of white rust as of 72 hours after salt water spraying was evaluated by the naked eye on the basis of the salt spray test method of JIS-Z-2371. The evaluation criteria are shown below (A to C are practical performance).

A: Little rust has occurred

B: The occurrence of a little rust is observed

C: The occurrence of rust is observed

D: The occurrence of rust is significant

15 [0131]

(4)-3: Corrosion resistance of processed portion

20 The situation of the occurrence of white rust as of 72 hours after salt water spraying was evaluated by the naked eye on the basis of the salt spray test method of JIS-Z-2371. The evaluation criteria are shown below (A to C are practical performance).

A: Little rust has occurred

B: The occurrence of a little rust is observed

C: The occurrence of rust is observed

D: The occurrence of rust is significant

25 [0132]

(5) Alkali resistance (post-degreasing corrosion resistance)

30 A test sheet was immersed for 2 minutes in a degreasing agent aqueous solution in which Fine Cleaner E6406 (manufactured by Nihon Parkerizing Co., Ltd.) was initially prepared at 20 g/L and the temperature was adjusted to 65°C, was washed with water, and was then dried at 80°C. The corrosion resistance of the sheet was evaluated using the conditions and the evaluation method for the corrosion

resistance of the flat surface portion described in (4)-1 above.

[0133]

2.3 Evaluation of external appearance

(6) Water condensation whitening resistance

5 One drop of ion-exchanged water was dropped onto a surface of a test sheet, and another test piece was superimposed on the water-dropped surface side in such a manner that the dry coating films faced each other; thus, a state where water was sandwiched by the two test pieces was created. Next, the test pieces were wrapped, four corners were fastened with clips, and the presence or absence of whitening of
10 the waterdrop-dropped portion after the test pieces were stored in a 50°C dryer for 72 hours was evaluated by visual inspection. The evaluation criteria are as follows (A and B are practical performance).

A: The visual inspection shows that there is no whitening and there is no dulling (gloss reduction), either

15 B: The visual inspection shows that there is no whitening but there is dulling (gloss reduction)

C: The visual inspection shows that there is whitening and there is also dulling (gloss reduction)

[0134]

20 (7) Stacking whitening resistance

5 to 10 pairs of test sheets, the test sheets of each of which pairs were opposed such that the coating surfaces faced each other, were stacked, four corners were bolted, and a torque wrench was used to apply a load up to a calibration mark of 5.7 N·m. Then, the stacked body was held for 6 days at a temperature of 70°C in
25 a humidity cabinet at a relative humidity of 80%, and was then taken out; and the whitening situation of a superimposed portion was assessed by visual inspection. The evaluation criteria are as follows (A to D are practical performance).

A: The area ratio of the whitened portion is less than 1% (there is no whitening)

B: The area ratio of the whitened portion is more than or equal to 1% and less than
30 5%

C: The area ratio of the whitened portion is more than or equal to 5% and less than

25%

D: The area ratio of the whitened portion is more than or equal to 25% and less than 50%

E: The area ratio of the whitened portion is more than or equal to 50%

5 [0135]

(8) Blackening resistance

A test sheet was held for 6 days at a temperature of 70°C in a humidity cabinet at a relative humidity of 80%, and was then taken out; and the blackening situation of the test sheet was assessed by visual inspection. The evaluation criteria are as follows (A to D are practical performance).

A: The area ratio of the blackened portion is less than 1% (there is no blackening)

B: The area ratio of the blackened portion is more than or equal to 1% and less than 5%

15 C: The area ratio of the blackened portion is more than or equal to 5% and less than 25%

D: The area ratio of the blackened portion is more than or equal to 25% and less than 50%

E: The area ratio of the blackened portion is more than or equal to 50%

[0136]

20 (9) Interference pattern

The external appearance of the steel sheet was observed by visual inspection under a sufficiently bright fluorescent lamp, and was evaluated in the following way.

A: As viewed from the front side, an interference pattern is clearly seen.

B: As viewed from the front side, an interference pattern is not seen.

25 C: As viewed from an oblique side, an interference pattern is not seen.

[0137]

(10) Filament tape resistance

A tape of FIRAMEN-TEPU (registered trademark) No. 9514 manufactured by Hitachi Maxell, Ltd. was adhered to a test sheet, and was then peeled off after holding for 7 days at a temperature of 40°C in a humidity cabinet at a relative humidity of 80%; and the evaluation of the external appearance was performed.

30

The evaluation criteria are as follows (A to D are practical performance).

A: The peeled portion is not seen at all even as viewed from an oblique side

B: The peeled portion is slightly seen as viewed from an oblique side

C: The peeled portion is distinctly seen as viewed from an oblique side

5 D: The peeled portion is slightly seen as viewed from the front side

E: The peeled portion is distinctly seen as viewed from the front side

[0138]

The results of the above are shown in Table 5 and Table 6.

[0139]

10 [Table 5]

No.	Evaluation											(10)
	Dry coating film condition			Corrosion resistance				External appearance				
	(1)	(2)	(3)	(4)			(5)	(6)	(7)	(8)	(9)	
				1	2	3						
Example 1	3	3	2	A	A	A	A	A	A	A	A	A
Example 2	3	2	2	A	A	A	A	A	A	A	A	A
Example 3	3	3	2	A	A	A	A	A	A	A	A	A
Example 4	3	3	2	A	A	A	A	A	A	A	A	A
Example 5	3	2	2	A	A	A	A	A	A	A	A	A
Example 6	3	3	2	A	A	A	A	A	A	A	A	A
Example 7	3	3	2	A	A	A	A	A	A	A	A	A
Example 8	3	2	2	A	A	A	A	A	A	A	A	A
Example 9	3	3	2	A	A	A	A	A	A	A	A	A
Example 10	3	3	2	A	A	A	A	A	A	A	A	A
Example 11	3	2	2	A	A	A	A	A	A	A	A	A
Example 12	3	3	2	A	A	A	A	A	A	A	A	A
Example 13	3	2	2	A	A	A	A	A	A	A	A	A
Example 14	3	3	2	A	A	A	A	A	A	A	A	A
Example 15	3	3	2	A	A	A	A	A	A	A	A	A
Example 16	3	2	2	A	A	A	A	A	A	A	A	A
Example 17	3	3	2	A	A	A	A	A	A	B	A	A
Example 18	3	3	2	A	A	A	A	A	A	A	A	A
Example 19	3	3	2	A	A	A	A	A	A	A	A	A
Example 20	3	3	2	A	A	A	A	A	A	A	A	A
Example 21	3	3	2	A	A	A	A	A	A	A	A	A
Example 22	3	3	2	A	A	A	A	A	A	A	A	A
Example 23	2	3	2	B	B	B	B	A	A	A	A	A
Example 24	3	2	2	B	B	B	B	A	A	A	A	A
Example 25	2	3	2	B	B	B	B	A	A	A	A	A
Example 26	3	2	2	B	B	B	B	A	A	A	A	A
Example 27	2	3	2	B	B	B	B	A	A	A	A	A

Example 28	3	2	2	B	B	B	B	A	A	A	A	A
Example 29	2	3	2	B	B	B	B	A	B	A	A	A
Example 30	3	2	2	B	B	B	B	A	A	A	A	A

[0140]

[Table 6]

No.	Evaluation											
	Dry coating film condition			Corrosion resistance				External appearance				(10)
	(1)	(2)	(3)	(4)			(5)	(6)	(7)	(8)	(9)	
				1	2	3						
Example 31	3	3	2	A	A	A	A	A	A	A	A	A
Example 32	3	3	2	A	A	A	A	A	A	A	A	A
Example 33	3	3	2	A	A	A	A	A	A	A	B	A
Example 34	3	3	2	A	A	A	A	A	A	A	A	A
Example 35	3	3	2	A	A	A	A	A	A	A	A	A
Example 36	3	3	2	A	A	A	A	A	A	A	A	A
Example 37	3	3	2	A	A	A	A	A	A	A	A	A
Example 38	3	3	2	A	A	A	A	A	A	A	A	A
Example 39	3	3	2	A	A	A	A	A	A	A	A	A
Example 40	3	3	2	A	A	A	A	A	A	A	A	A
Example 41	3	3	2	A	A	A	B	A	A	A	A	A
Example 42	3	3	2	A	A	A	A	A	A	A	A	A
Example 43	3	3	2	A	A	A	A	A	A	A	A	A
Example 44	3	3	2	A	A	A	B	A	A	A	A	A
Example 45	3	2	2	A	B	A	B	A	A	A	A	A
Example 46	2	3	2	A	A	A	A	A	A	A	C	A
Example 47	2	3	2	B	C	D	D	A	A	A	C	A
Comparative Example 1	2	1	1	A	D	C	A	A	A	A	A	A
Comparative Example 2	2	1	1	A	D	C	A	A	A	A	A	A
Comparative Example 3	1	1	2	A	A	D	A	B	A	A	A	A
Comparative Example 4	1	3	2	A	D	A	B	A	B	A	A	A
Comparative Example 5	2	2	2	C	D	D	D	A	A	A	A	A
Comparative Example 6	2	2	2	C	D	D	D	A	A	A	A	A
Comparative Example 7	2	2	2	C	D	D	D	A	A	A	A	A
Comparative Example 8	2	1	2	C	D	D	D	C	E	A	A	E
Comparative Example 9	2	1	2	C	C	C	C	B	E	A	A	E
Comparative Example 10	2	2	2	C	C	C	C	A	A	E	A	A
Comparative Example 11	2	1	2	C	D	D	D	C	E	A	A	E
Comparative Example 12	2	1	2	C	D	D	D	C	E	A	A	E
Comparative Example 13	2	2	2	C	D	D	D	C	B	A	A	A
Comparative Example 14	2	1	2	C	D	D	D	C	E	A	A	E
Comparative Example 15	-	-	-	D	D	D	D	A	A	E	A	A

[0141]

As shown in Table 5 and Table 6, in all of the surface-treated steel sheets
5 according to Examples 1 to 45, which are Examples of the present invention, the

evaluation in (6) the water condensation whitening resistance, (7) the stacking whitening resistance, (8) the blackening resistance, and (9) the interference pattern in addition to (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) was good. Further, all of the surface-treated steel sheets according to Examples 1 to 45, which are Examples of the present invention, were excellent also in (10) the filament tape resistance.

[0142]

As shown in Table 6, in Example 46, in which the surface roughness (Ra-S) of the steel sheet was less than 0.1 μm , (6) the water condensation whitening resistance and (7) the stacking whitening resistance in addition to (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were excellent, but (9) an interference pattern was observed. In Example 47, in which the surface roughness (Ra-S) of the steel sheet was more than 2 μm , (9) an interference pattern was observed.

[0143]

In Comparative Example 1, in which the average particle size of the polyurethane resin was less than 20 nm, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, (3) the surface roughness (Ra-F) of the dry coating film was more than 10 nm, and the dispersion of resin particles was non-uniform; consequently, (4) the corrosion resistance was insufficient.

In Comparative Example 2, in which the average particle size of the polyurethane resin was more than 200 nm, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, (3) the surface roughness (Ra-F) of the dry coating film was more than 10 nm, and the dispersion of resin particles was non-uniform; consequently, (4) the corrosion resistance was insufficient.

[0144]

In Comparative Example 3, in which (1) the area ratio of the resin component in the cross section of the dry coating film was less than 35%, (4) the maximum value of the distance between the centers of gravity of resin particles was

more than 3.0 times the average particle size, the dispersion of resin particles was non-uniform, and (4) the corrosion resistance was insufficient.

In Comparative Example 4, in which (1) the area ratio of the resin component in the cross section of the dry coating film was more than 80%, the effect
5 of improving corrosion resistance based on Ti, V, and Si was not obtained sufficiently, and (4) the corrosion resistance was insufficient.

[0145]

In Comparative Example 5 not containing Si, (4) the corrosion resistance was insufficient.

10 In Comparative Example 6 not containing Ti, (4) the corrosion resistance was insufficient.

In Comparative Example 7 not containing V, (4) the corrosion resistance was insufficient.

[0146]

15 In Comparative Example 8 not containing P, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, and the dispersion of resin particles was non-uniform; consequently, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient. Further, in Comparative
20 Example 8, (7) the stacking whitening resistance, (6) the water condensation whitening resistance, and (10) the filament tape resistance did not satisfy practical performance.

[0147]

In Comparative Example 9, in which the P content was small, (2) the
25 maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, and the dispersion of resin particles was non-uniform; consequently, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were low. Further, in Comparative
Example 9, (7) the stacking whitening resistance and (10) the filament tape resistance
30 did not satisfy practical performance.

[0148]

In Comparative Example 10, in which the P content was large, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were low, and (8) the blackening resistance did not satisfy practical performance.

5 [0149]

In Comparative Example 11, in which the acetic acid component (G) and the phosphoric acid component (H) were not used in the surface treatment agent, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, and the dispersion of resin particles was non-uniform; consequently, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient. Further, in Comparative Example 11, (7) the stacking whitening resistance and (10) the filament tape resistance did not satisfy practical performance.

[0150]

15 In Comparative Example 12, in which the titanium compound (D) and the phosphoric acid component (H) were not used in the surface treatment agent, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, the dispersion of resin particles was non-uniform, and the titanium compound (D) was not contained; consequently, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient. Further, in Comparative Example 12, (7) the stacking whitening resistance and (10) the filament tape resistance did not satisfy practical performance.

[0151]

25 In Comparative Example 13, in which the titanium compound (D) and the acetic acid component (G) were not used in the surface treatment agent, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient.

[0152]

30 In Comparative Example 14, in which the titanium compound (D), the acetic acid component (G), and the phosphoric acid component (H) were not used in

the treatment agent, (2) the maximum value of the distance between the centers of gravity of resin particles was more than 3.0 times the average particle size, the dispersion of resin particles was non-uniform, and the titanium compound (D) was not contained; consequently, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient. Further, in Comparative Example 14, (7) the stacking whitening resistance and (10) the filament tape resistance did not satisfy practical performance.

[0153]

In Comparative Example 15, in which a dry coating film was not formed, (4) the corrosion resistance and (5) the alkali resistance (post-degreasing corrosion resistance) were insufficient. Further, the steel sheet according to Comparative Example 15 did not have practical performance for (8) the blackening resistance.

[0154]

A cross section of the surface-treated steel sheet of Example 4 was observed with a scanning transmission electron microscope (STEM), and a bright field (STEM-BF) image and a high-angle annular dark field (STEM-HAADF) image were obtained. FIG. 4 is a bright field image of Example 4. FIG. 5 is a high-angle annular dark field image of Example 4.

[0155]

In the bright field (STEM-BF) image of Example 4 shown in FIG. 4, it can be seen that a dry coating film composed of a gray portion and a plurality of substantially spherical white portions is observed and that white portions are arranged substantially uniformly in the dry coating film. The white portion in FIG. 4 is black in the high-angle annular dark field (STEM-HAADF) image of Example 4 shown in FIG. 5. Light elements are black in the high-angle annular dark field image, and therefore the white portion shown in FIG. 4 is a resin particle. From this, it has been found that, in the surface-treated steel sheet of Example 4, resin particles are dispersed substantially uniformly in the dry coating film.

[0156]

Further, a high-angle annular dark field (STEM-HAADF) image in which a cross section of the surface-treated steel sheet of Example 4 is observed with a

scanning transmission electron microscope (STEM) is shown. A schematic pseudo shape of a resin particle is shown by the edge of a solid line. Further, an imaginary resin particle having the average particle size is shown by a broken line.

[0157]

5 In the high-angle annular dark field (STEM-HAADF) image of Example 4 shown in FIG. 6, it has been found that, in the surface-treated steel sheet of Example 4, resin particles are dispersed substantially uniformly in the dry coating film. Further, it has been found that the distance between the centers of gravity of resin particles is less than or equal to 3 times the particle size.

10 [0158]

Further, a cross section of the surface-treated steel sheet of Comparative Example 11 was observed with a scanning transmission electron microscope (STEM), and bright field (STEM-BF) images were obtained. FIG. 7 and FIG. 8 are bright field images of Comparative Example 11. A schematic pseudo shape of a resin particle is shown by the edge of a solid line. Further, an imaginary resin particle having the average particle size is shown by a broken line.

[0159]

In the bright field (STEM-BF) image of Comparative Example 11 shown in FIG. 7, a dry coating film composed of a gray portion and a plurality of substantially spherical white portions was observed, and white portions were arranged to exist locally in the dry coating film. From this, it has been found that resin particles in the dry coating film exist locally in the surface-treated steel sheet of Comparative Example 11. Further, FIG. 8 is an enlarged image of the portion surrounded by the frame of FIG. 7, and it has been found that the distance between the centers of gravity of resin particles is more than 3 times the particle size.

25

[0160]

Further, a surface-treated steel sheet of a comparative example that was the same as Example 4 except that a dry coating film in which acrylic resin particles were used as resin particles was formed was produced. Then, a cross section of the surface-treated steel sheet of the comparative example was observed with a scanning transmission electron microscope (STEM), and a bright field (STEM-BF) image was

30

obtained in a similar manner to Example 4. As a result, in the bright field (STEM-BF) image of the comparative example, a dry coating film composed of a gray portion and a plurality of substantially spherical white portions was observed, and white portions were arranged to exist locally in the dry coating film. From this, it

5 has been found that resin particles in the dry coating film exist locally in the surface-treated steel sheet of the comparative example.

[0161]

The preferable embodiment of the present invention has been described above, but the present invention is not limited to the above-mentioned embodiment.

10 That is, it is understood that other forms or various modified examples which can be conceived by a person skilled in the art within the scope of the invention described in the claims also belong to the technical scope of the present invention.

Reference Signs List

15 [0162]

- 1 steel sheet
- 2 plating layer
- 3, 3A dry coating film
- 10 surface-treated steel sheet
- 20 31 first component
- 311, 311A resin particle
- 32 second component

CLAIMS

Claim 1

- A surface-treated steel sheet comprising:
a steel sheet;
5 a plating layer containing zinc and formed on a surface of the steel sheet;
and
a dry coating film formed on the plating layer,
wherein the dry coating film contains a resin component containing resin
particles made of a polyurethane resin with an average particle size of more than or
10 equal to 20 nm and less than or equal to 200 nm, P, Ti, V, and Si,
the dry coating film contains P at more than or equal to 2.5 mass% and less
than or equal to 7.5 mass% on a phosphoric acid basis,
an area ratio of the resin component in a cross section of the dry coating
film is more than or equal to 35% and less than or equal to 80%,
15 the resin particles are dispersed in the dry coating film, and
a maximum value of a distance between centers of gravity of resin particles
is less than or equal to 3.0 times an average particle size of the resin particle.

Claim 2

- 20 The surface-treated steel sheet according to claim 1,
wherein a surface roughness (Ra) of the dry coating film is more than or
equal to 1 nm and less than or equal to 10 nm.

Claim 3

- 25 The surface-treated steel sheet according to claim 1 or 2,
wherein a surface roughness (Ra) of the steel sheet is more than or equal to
0.1 μm and less than or equal to 2 μm .

Claim 4

- 30 The surface-treated steel sheet according to any one of claims 1 to 3,
wherein the plating layer contains antimony.

Claim 5

The surface-treated steel sheet according to any one of claims 1 to 4,
wherein the resin component contains olefin-based wax and/or a phenolic
5 resin.

Claim 6

The surface-treated steel sheet according to any one of claims 1 to 5,
wherein the dry coating film contains
10 Si at more than or equal to 10 mass% and less than or equal to 40
mass% on a SiO₂ basis,
Ti at more than or equal to 1.7 mass% and less than or equal to 2.4
mass%, and
V at more than or equal to 0.70 mass% and less than or equal to
15 0.90 mass%, and
a mass ratio between Ti and V (Ti/V) is more than or equal to 2.1 and less
than or equal to 2.9.