

[Document Type] Specification

[Title of the Invention]

Zn-BASED PLATED STEEL SHEET

[Technical Field]

5 [0001]

The present invention relates to a Zn-based plated steel sheet.

Priority is claimed on Japanese Patent Application No. 2020-176149, filed on October 20, 2020, the content of which is incorporated herein by reference.

[Background Art]

10 [0002]

There are Zn-based plated steel sheets as plated steel sheets that are much used and have favorable corrosion resistance. Zn-based plated steel sheets are used in various manufacturing industries such as automobiles, home appliances, and building materials. Among these, the use of Al-added plating has been increasing in recent years because of its high corrosion resistance.

[0003]

As an example of a Zn-based plated steel sheet developed for the purpose of improving corrosion resistance, Patent Document 1 discloses a hot-dip Zn-Al-Mg-Si-plated steel sheet. Since this plated steel sheet has a pear skin-like appearance, it has excellent external beautifulness.

[0004]

Incidentally, conventionally, chromate treatment using hexavalent chromate or the like is widely performed after plating in order to impart a further advanced anti-rust function to Zn-based plated steel sheets. Furthermore, in order to impart high-value-added functions such as designability, stain resistance, and lubricity, coating with an

organic resin has been carried out as necessary. However, due to the background of increasing environmental problems, there is a movement to refrain from using chromate treatment. Therefore, there is a surface-treated plated steel sheet disclosed in Patent Document 2 below for the purpose of easily imparting an advanced anti-rust function
5 with only a single-layer treatment with a resin-based film without performing chromate treatment.

[0005]

By using the film disclosed in Patent Document 2, it is possible to further improve the corrosion resistance. However, Zn-based plated steel sheets containing Al
10 have a problem that, when stored for a long period of time, the plated surface partially or wholly turns black due to oxidation of Al contained in the plated layer.

[Citation List]

[Patent Documents]

[0006]

15 [Patent Document 1]

Japanese Patent No. 3179446

[Patent Document 2]

Japanese Unexamined Patent Application, First Publication No. 2006-52462

[Summary of the Invention]

20 [Problems to be Solved by the Invention]

[0007]

The present invention has been made from the viewpoint of the above-described circumstances, and an object of the present invention is to provide a Zn-based plated steel sheet which contains Al and has improved corrosion resistance and weather resistance

and in which, even if a plated surface partially or wholly turns black, the blackening is inconspicuous and the metallic appearance can be maintained.

[Means for Solving the Problem]

[0008]

5 In order to solve the above-described problem, the present inventors have conducted extensive studies and found that by incorporating a pigment into a chemical conversion treatment layer, the black discoloration on the surface of the plated layer is made less noticeable and the metallic appearance of the surface of the plated layer is not impaired. The present invention employs the following configuration.

10 [0009]

 [1] A Zn-based plated steel sheet including: a steel sheet; a Zn-based plated layer which contains Zn and 0.05 to 60 mass% of Al and is placed on at least one surface of the steel sheet; and a chromate-free chemical conversion treatment layer which has a deposition amount of 0.1 to 15 g/m² per surface and is placed on the Zn-based plated
15 layer, in which the chemical conversion treatment layer contains 20 mass% or more of a resin, 1 to 20 mass% of silica particles having an average particle diameter of 5 to 200 nm, a pigment containing one or more of Cu, Co, or Fe, b* of an appearance of the Zn-based plated steel sheet evaluated in a CIE 1976 (L*, a*, b*) color space is -30 to -2, a 60-degree mirror surface glossiness G_s (60°) specified in JIS Z 8741:1997 is 50 to 200, and
20 the Zn-based plated steel sheet exhibits a metallic appearance.

 [2] The Zn-based plated steel sheet according to [1], in which the pigment is any one or more of copper(II) phthalocyanine, cobalt(II) phthalocyanine, copper sulfate, cobalt sulfate, iron sulfate, and iron oxide.

 [3] The Zn-based plated steel sheet according to [1] or [2], in which
25 [Si]/([Cu]+[Co]+[Fe]) is within a range of 1 to 200 as a mixing ratio between the silica

particles and the pigment in the chemical conversion treatment layer in a case where an equivalent amount of Si in the silica particles is represented by [Si] and equivalent amounts of Cu, Co, and Fe in the pigment are respectively represented by [Cu], [Co], and [Fe].

5 [4] The Zn-based plated steel sheet according to any one of [1] to [3], in which an arithmetic average roughness Ra of the Zn-based plated layer is 0.5 to 2.0 μm and an arithmetic average height Sa of the chemical conversion treatment layer is 5 nm to 100 nm.

 [5] The Zn-based plated steel sheet according to any one of [1] to [4], in which
10 the chemical conversion treatment layer further contains either one or both of an Nb compound and a phosphoric acid compound.

 [6] The Zn-based plated steel sheet according to any one of [1] to [5], in which the resin in the chemical conversion treatment layer includes any one or more of a polyolefin resin, a fluororesin, an acrylic resin, a urethane resin, a polyester resin, an
15 epoxy resin, and a phenol resin.

 [7] The Zn-based plated steel sheet according to any one of [1] to [6], in which the Zn-based plated layer contains 4 mass% to 22 mass% of Al, 1 mass% to 10 mass% of Mg, and the balance being Zn and impurities in an average composition.

 [8] The Zn-based plated steel sheet according to any one of [1] to [7], in which
20 the Zn-based plated layer further contains 0.0001 to 2 mass% of Si in an average composition.

 [9] The Zn-based plated steel sheet according to any one of [1] to [8], in which the Zn-based plated layer further contains one or more of Ni, Sb, and Pb in a total of 0.0001 to 2 mass% in an average composition.

[10] The Zn-based plated steel sheet according to any one of [1] to [9], in which a non-pattern portion and a pattern portion placed to have a predetermined shape are formed on the Zn-based plated layer, the pattern portion and the non-pattern portion each contain one or two of a first region and a second region determined by any of

- 5 determination methods 1 to 5 below, and an absolute value of a difference between an area proportion of the first region in the pattern portion and an area proportion of the first region in the non-pattern portion is 30% or more.

(Determination method 1)

- Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals
10 of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region partitioned by the virtual grid lines is defined as a measurement region A, and an L^* -value in each measurement region A is measured. When arbitrary 50 points are selected from the obtained L^* -values and an average of the obtained L^* -values at the 50 points is defined as a standard L^* -value, a region in which the L^* -value is equal to or more than
15 the standard L^* -value is defined as a first region and a region in which the L^* -value is less than the standard L^* -value is defined as a second region.

(Determination method 2)

- Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region
20 partitioned by the virtual grid lines is defined as a measurement region A, an L^* -value in each measurement region A is measured, a region in which the L^* -value is 45 or more is defined as a first region, and a region in which the L^* -value is less than 45 is defined as a second region.

(Determination method 3)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, and an arithmetic average height Sa_2 is measured in each of a plurality of regions partitioned by the virtual grid lines. A region in which the obtained arithmetic average height Sa_2 is 1 μm or more is defined as a first region, and a region in which the obtained arithmetic average height Sa_2 is less than 1 μm is defined as a second region.
(Determination method 4)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a plane (0002) of a Zn phase and a diffraction peak intensity I_{10-11} of a plane (10-11) of the Zn phase are measured for each region through an X-ray diffraction method in which X-rays are respectively made to be incident on the plurality of regions partitioned by the virtual grid lines, and a proportion of these intensities (I_{0002}/I_{10-11}) is defined as an orientation rate. A region in which the orientation rate is 3.5 or more is defined as a first region, and a region in which the orientation rate is less than 3.5 is defined as a second region.
(Determination method 5)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm, and a circle S centered at a centroid point G of each region is drawn for each of a plurality of regions partitioned by the virtual grid lines. A diameter R of the circle S is set so that a total length of surface boundary lines of the Zn-based plated layer contained in the circle S is 10 mm. An average value of a maximum diameter R_{max} and a minimum diameter R_{min} among diameters R of circles S in the plurality of regions is defined as a standard diameter R_{ave} , a region having a circle S of which the diameter R is less than the standard diameter R_{ave} is defined as a first region, and a region having a circle S of which the diameter R is greater than or equal to the standard diameter R_{ave} is defined as a second region.

[11] The Zn-based plated steel sheet according to any one of [1] to [10], in which the Zn-based plated layer has any one or more of Co, Fe, and Ni on its surface.

[Effects of the Invention]

[0010]

5 According to the present invention, it is possible to provide a Zn-based plated steel sheet which contains Al and in which, even if a plated surface partially or wholly turns black due to oxidation of Al contained in the plated layer, the blackening can be made less noticeable to maintain the metallic appearance, and corrosion resistance and weather resistance are improved.

10 [Embodiment for Implementing the Invention]

[0011]

 The present inventors have found that by coloring a chemical conversion treatment layer blue by incorporating a pigment into the chemical conversion treatment layer, black discoloration caused on the surface of the plated layer is made less
15 noticeable. However, if the blue color is too dark, the metallic appearance of the surface of the plated layer is less likely to be visually recognized. In addition, it has been found that the visibility of the black discoloration and the visibility of the metallic appearance change depending on whether incident light is reflected from the surface of the plated layer or the surface of the chemical conversion treatment layer. As a result of
20 further investigation, it has been found that by controlling a b^* -value when evaluation is carried out in a CIE 1976 (L^* , a^* , b^*) color space and a 60-degree mirror surface glossiness G_s (60°) specified in JIS Z 8741:1997 such that they become within predetermined ranges, the black discoloration caused on the surface of the plated layer can be made less noticeable and the metallic appearance can be visually recognized. In
25 addition, it has also been found that by controlling the b^* -value and the 60-degree mirror

surface glossiness G_s (60°), even in a case where an arbitrary shape such as a letter is displayed on the surface of the plated layer, the arbitrary shape is likely to be seen.

[0012]

That is, the Zn-based plated steel sheet of an embodiment of the present invention is a Zn-based plated steel sheet including: a steel sheet; a Zn-based plated layer which contains Zn and 0.05 to 60 mass% of Al and is placed on at least one surface of the steel sheet; and a chromate-free chemical conversion treatment layer which has a deposition amount of 0.1 to 15 g/m^2 per surface and is placed on the Zn-based plated layer, in which the chemical conversion treatment layer contains 20 mass% or more of a resin, 1 to 20 mass% of silica particles having an average particle diameter of 5 to 200 nm, and a pigment containing one or more of Cu, Co, or Fe, b^* in a case where an appearance of the Zn-based plated steel sheet is evaluated in a CIE 1976 (L^* , a^* , b^*) color space is -30 to -2, a 60-degree mirror surface glossiness G_s (60°) specified in JIS Z 8741:1997 is 50 to 200, and the Zn-based plated steel sheet exhibits a metallic appearance.

In addition, in the Zn-based plated steel sheet of the present embodiment, it is preferable that the pigment be any one or more of copper(II) phthalocyanine, cobalt(II) phthalocyanine, copper sulfate, cobalt sulfate, iron sulfate, and iron oxide.

In addition, in the Zn-based plated steel sheet of the present embodiment, it is preferable that $[\text{Si}]/([\text{Cu}]+[\text{Co}]+[\text{Fe}])$ be within a range of 1 to 200 as a mixing ratio between the silica particles and the pigment in the chemical conversion treatment layer in a case where an equivalent amount of Si in the silica particles is represented by $[\text{Si}]$ and equivalent amounts of Cu, Co, and Fe in the pigment are respectively represented by $[\text{Cu}]$, $[\text{Co}]$, and $[\text{Fe}]$. Each unit of equivalent amounts of Si, Cu, Co, and Fe is “ g/m^2 ”.

In addition, in the Zn-based plated steel sheet of the present embodiment, it is preferable that an arithmetic average roughness Ra of the Zn-based plated layer be 0.5 to 2.0 μm and an arithmetic average height Sa of the chemical conversion treatment layer be 5 nm to 100 nm.

5 [0013]

[Zn-based plated steel sheet]

Hereinafter, the Zn-based plated steel sheet of the present embodiment will be described.

The material of the steel sheet that serves as an underlayer of the Zn-based
10 plated layer is not particularly limited. As the material, general steel or the like can be used without particular limitation, and Al-killed steel or some high-alloy steels can also be used. The shape is also not particularly limited. By applying a hot-dip plating method to be described below to a steel sheet, the Zn-based plated layer according to the present embodiment is formed.

15 [0014]

[Zn-based plated layer]

Next, chemical components of the Zn-based plated layer will be described.

The Zn-based plated layer preferably contains Zn and 0.05 to 60 mass% of Al and more preferably contains 0.05 to 60 mass% of Al with the balance being Zn and
20 impurities. By incorporating 0.05 mass% or more of Al, corrosion resistance of the Zn-based plated layer can be improved. In addition, by setting the amount of Al to 60 mass% or less, the amount of Zn contained in the Zn-based plated layer can be relatively increased to ensure sacrificial corrosion protection properties. The Zn-based plated layer may contain 40 mass% or more of Zn.

25 [0015]

In addition, the Zn-based plated layer of the present embodiment may contain 4 to 22 mass% of Al, 1 to 10 mass% of Mg, and the balance being Zn and impurities in an average composition. In addition, the Zn-based plated layer may contain 0.0001 to 2 mass% of Si in an average composition.

5 [0016]

Hereinafter, the reasons for limiting the composition of the Zn-based plated layer containing 4 to 22 mass% of Al, 1 to 10 mass% of Mg, and the balance being Zn and impurities will be described below.

[0017]

10 The amount of Al is within the range of 4 to 22 mass%. Al is preferably contained to ensure corrosion resistance. If the amount of Al in the Zn-based plated layer is 4 mass% or more, the effect of improving corrosion resistance is further enhanced. When the amount of Al is 22 mass% or less, the effect of improving corrosion resistance and weather resistance while maintaining a metallic appearance is
15 likely to be secured.

[0018]

The amount of Mg is within the range of 1 to 10 mass%. Mg is preferably contained to improve corrosion resistance. If the amount of Mg in the Zn-based plated layer is 1 mass% or more, the effect of improving corrosion resistance is further
20 enhanced. When the amount of Mg is 10 mass% or less, generation of dross in a plating bath is suppressed, thereby suppressing generation of sites where plating is not formed normally due to the dross adhering to the plating, and deterioration in corrosion resistance can be suppressed.

[0019]

The amount of Mg may be 0%. That is, the Zn-based plated layer of the Zn-based plated steel sheet of the present embodiment is not limited to a Zn-Al-Mg-based hot-dip plated steel sheet and may be a Zn-Al-based hot-dip plated layer.

[0020]

5 In addition, the Zn-based plated layer may contain Si within a range of 0.0001 to 2 mass%.

Since Si may improve adhesion of the Zn-based plated layer, Si may be incorporated. By incorporating 0.0001 mass% or more of Si, preferably 0.001% or more of Si, and more preferably 0.01% or more of Si, the effect of improving adhesion is
10 exhibited. Therefore, 0.0001 mass% or more of Si is preferably incorporated. On the other hand, even if the amount of Si incorporated exceeds 2 mass%, the effect of improving plating adhesion is saturated, and therefore, the amount of Si is set to 2 mass% or less. From the viewpoint of plating adhesion, the amount of Si may be within a range of 0.001 to 1 mass% or a range of 0.01 to 0.8 mass%.

15 [0021]

The Zn-based plated layer may contain one or more of Ni, Sb, and Pb in a total of 0.0001 to 2 mass%, preferably 0.001 to 2 mass% in an average composition. By incorporating these elements, the corrosion resistance can be further improved.

[0022]

20 The balance with respect to the chemical component of the Zn-based plated layer is zinc (Zn) and impurities. Impurities include those that are unavoidably contained in zinc and other base metals and those that are introduced by dissolution of steel in a plating bath.

[0023]

The average composition of the Zn-based plated layer can be measured through the following method. First, a chemical conversion treatment layer is removed with a coating film remover that does not corrode plating (for example, Neorever SP-751 manufactured by Sansai Kako Co., Ltd.). In a case where a surface layer coating film exists on the chemical conversion treatment layer, the surface layer coating film is also removed. Thereafter, the Zn-based plated layer is dissolved in hydrochloric acid containing an inhibitor (for example, Hibiron manufactured by Sugimura Chemical Industrial Co., Ltd.), and the resulting solution is subjected to inductively coupled plasma (ICP) emission spectroscopic analysis.

10 [0024]

Furthermore, the surface of the Zn-based plated layer preferably contains one or more elements selected from Co, Fe, and Ni. Co, Fe, and Ni adhere to the surface of the Zn-based plated layer by performing Co treatment, Fe treatment, or Ni treatment after forming the Zn-based plated layer. By having these elements on the surface of the Zn-based plated layer, blackening resistance can be improved. Co, Fe, or Ni preferably exists on the surface of the Zn-based plated layer in the form of a compound.

[0025]

[Chemical conversion treatment layer]

Next, the chemical conversion treatment layer will be described. The chemical conversion treatment layer of the present embodiment contains 20 mass% or more of a resin, 1 to 20 mass% of silica particles having an average particle diameter of 5 to 200 nm, and a pigment containing one or more of Cu, Co, or Fe. The chemical conversion treatment layer of the present embodiment is a film obtained by applying an aqueous composition containing a resin, silica particles, and a pigment to a Zn-based plated layer formed on a steel sheet and drying it.

[0026]

[Resin]

A resin contained in the chemical conversion treatment layer may be any general resin, and examples thereof include a polyolefin resin, a fluorine resin, an acrylic resin, a urethane resin, a polyester resin, an epoxy resin, and a phenol resin. These resins may be water-soluble resins or may be resins (water-dispersible resins) that are inherently water-insoluble but can be finely dispersed in water like emulsions or suspensions. In addition to the water-soluble resins, the resins (water-dispersible resins) that are inherently water-insoluble but can be finely dispersed in water like emulsions or suspensions are referred to as resins. In particular, it is preferable that resins include at least one of a polyolefin resin, a fluorine resin, an acrylic resin, and a phenol resin for excellent weather resistance.

[0027]

The polyolefin resin is not particularly limited, and examples thereof include one obtained by subjecting ethylene and unsaturated carboxylic acids such as methacrylic acid, acrylic acid, maleic acid, fumaric acid, itaconic acid, and crotonic acid to radical polymerization at a high temperature and under a high pressure, and then neutralizing the resultant with ammonia, amine compounds, metal compounds such as KOH, NaOH, LiOH, or amine compounds or ammonia containing the above-described metal compounds and dispersing the resultant in water.

[0028]

The fluorine resin is not particularly limited, and examples thereof include a homopolymer or copolymer of a fluoroolefin. Examples of copolymers include a copolymer of a fluoroolefin and a fluorine atom-free monomer and/or a fluorine-containing monomer other than a fluoroolefin.

[0029]

The acrylic resin is not particularly limited, and examples thereof include one obtained by subjecting unsaturated monomers such as styrene, alkyl (meth)acrylates, (meth)acrylic acid, hydroxyalkyl (meth)acrylates, and alkoxysilane (meth)acrylates to
5 radical polymerization using a polymerization initiator in an aqueous solution. The above-described polymerization initiator is not particularly limited, and persulfates such as potassium persulfate and ammonium persulfate and azo compounds such as azobiscyanovaleric acid and azobisisobutyronitrile can be used, for example.

[0030]

10 The urethane resin is not particularly limited, and examples thereof include one obtained by reacting polyhydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,6-hexanediol, neopentyl glycol, triethylene glycol, bisphenol hydroxypropyl ether, glycerin, trimethylolethane, and trimethylolpropane with diisocyanate compounds such as hexamethylene diisocyanate, isophorone diisocyanate,
15 and tolylene diisocyanate, extending chains with diamines or the like, and dispersing the reactant in water.

[0031]

The polyester resin is not particularly limited, and examples thereof include one obtained by subjecting polyhydric alcohols such as ethylene glycol, propylene glycol,
20 diethylene glycol, 1,6-hexanediol, neopentyl glycol, triethylene glycol, bisphenol hydroxypropyl ether, glycerin, trimethylolethane, and trimethylolpropane and polybasic acids such as phthalic anhydride, isophthalic acid, terephthalic acid, succinic anhydride, adipic acid, sebacic acid, maleic anhydride, itaconic acid, fumaric acid, and hymic anhydride to dehydration condensation, neutralizing the resultant with ammonia or amine
25 compounds, and dispersing the resultant in water.

[0032]

The epoxy resin is not particularly limited, and examples thereof include: one obtained by reacting epoxy resins such as a bisphenol A-type epoxy resin, a bisphenol F-type epoxy resin, a resorcin-type epoxy resin, a hydrogenated bisphenol A-type epoxy resin, a hydrogenated bisphenol F-type epoxy resin, a resorcin-type epoxy resin, and a novolac-type epoxy resin with amine compounds such as diethanolamine and N-methylethanolamine and neutralizing the reactant with an organic acid or an inorganic acid; and one obtained by subjecting a high-acid value acrylic resin to radical polymerization in the presence of the above-described epoxy resins, and then neutralizing the resultant with ammonia or amine compounds and dispersing the resultant in water.

[0033]

The phenol resin is not particularly limited, and examples thereof include one obtained by reacting amine compounds such as diethanolamine and N-methylethanolamine with phenol resins such as a methylolated phenol resin obtained by subjecting formaldehyde and aromatic compounds such as phenols, resorcin, cresols, bisphenol A, and para-xylene dimethyl ether to addition reaction in the presence of a reaction catalyst, and neutralizing the reactant with an organic acid or an inorganic acid.

[0034]

The resin is contained in the chemical conversion treatment layer at a rate of 20 mass% or more. By setting the amount of resin to 20 mass% or more, the chemical conversion treatment layer itself does not become brittle and the Zn-based plated layer can be stably coated. The chemical conversion treatment layer may contain, in addition to a resin, silica particles, and a pigment, components such as Nb compounds and phosphoric compounds other than the resin, and the amount of resin may be the balance with respect to these components.

[0035]

[Silica particles]

Silica particles are incorporated to improve corrosion resistance of the chemical conversion treatment layer. Silica particles having an average particle diameter in a range of 5 to 200 nm are suitable. The silica particles are contained in the chemical conversion treatment layer at a rate of 1 to 20 mass%. By setting the amount of silica particles to 1 mass% or more, an effect of improving corrosion resistance can be obtained. In addition, by setting the amount of silica particles to 20 mass% or more, the chemical conversion treatment layer itself does not become brittle and the Zn-based plated layer can be stably coated. It is difficult to obtain silica particles having an average particle diameter of less than 5 nm, and it is practically difficult to prepare and produce a chemical conversion treatment layer containing silica particles having an average particle diameter of less than 5 nm. Therefore, the lower limit of the average particle diameter of the silica particles is set to 5 nm or more. In addition, if the average particle diameter of the silica particles exceeds 200 nm, there is a concern that the chemical conversion treatment layer will become cloudy, thereby impairing the metallic appearance of the Zn-based plated layer. From the viewpoint of maintaining both corrosion resistance and strength of the chemical conversion treatment layer, the amount of silica particles is more preferably 3 to 15 mass% in the chemical conversion treatment layer.

[0036]

Since inorganic pigments such as silica particles generally have a small particle diameter, they may exist in the chemical conversion treatment layer in the form of secondary particles having a larger particle diameter than the primary particle diameter. The particle diameter of the secondary particles (particles in which inorganic pigments

aggregate) is referred to as a “secondary particle diameter” below. The silica particles in the present embodiment may be a mixture of primary particles and secondary particles, and even if primary particles and secondary particles coexist, both may have an average particle diameter in a range of 5 to 200 nm. The average particle diameter of the silica particles is more preferably 5 to 150 nm from the viewpoint of maintaining high permeability of the chemical conversion treatment layer.

[0037]

The average particle diameter of silica in the chemical conversion treatment layer is measured through the following method. First, a thin film specimen of a chemical conversion treatment layer is prepared through a microtome method so that a cross section perpendicular to the rolling direction of the steel sheet of the present invention can be observed. In a $20\ \mu\text{m} \times t\ \mu\text{m}$ region of the obtained thin film specimen (a region with $20\ \mu\text{m}$ in the direction parallel to the plate width direction and a thickness of $t\ \mu\text{m}$ in the plate thickness direction), a 200 kV field emission transmission electron microscope (FE-TEM) was used to observe at least 5 regions at a magnification of 100,000 times. Equivalent circle diameters of all the silica particles in the observation region are calculated using Equation 1 below and respectively defined as particle diameters of the silica particles, and the average particle diameter is obtained by averaging the particle diameters.

[0038]

Equivalent circle diameter = $2\sqrt{S/\pi}$... Equation 1

However, S is the area of the silica particles, and π is a circular constant.

[0039]

The amount of silica particles in the chemical conversion treatment layer is

measured through the following method. First, a plurality of comparative samples having a chemical conversion treatment layer with a known silica particle content are prepared separately from a target sample, surfaces thereof are measured with a fluorescent X-ray device, and a calibration curve is drawn from the relationship between the amount of silica particles and the obtained detection intensity of Si. Next, the target sample is measured with a fluorescent X-ray device under the same conditions as those of the comparative samples, and the amount of silica particles is obtained using the above-described calibration curve from the obtained detection intensity of Si.

[0040]

In addition, in the present invention, since the average particle diameter of the water-dispersed silica before being dispersed in a coating material is maintained even in the chemical conversion treatment layer, such a value may be used.

[0041]

In addition to silica particles, titania particles, alumina particles, zirconia particles, and the like may be contained to improve corrosion resistance of the chemical conversion treatment layer.

[0042]

[Pigment]

The chemical conversion treatment layer contains a pigment containing one or more of Cu, Co, or Fe. The pigment may contain one of Cu, Co, or Fe or may contain two or more thereof. In addition, the chemical conversion treatment layer may contain one or more pigments containing one or more of Cu, Co, or Fe. Examples of pigments include copper (II) phthalocyanine, cobalt (II) phthalocyanine, copper sulfate, cobalt sulfate, iron sulfate, and iron oxide. By incorporating pigments into the chemical conversion treatment layer, the chemical conversion treatment layer is colored blue, and

black discoloration appearing on the surface of the plated layer is made less noticeable.

In order to obtain this effect, the amount of pigment in the chemical conversion treatment layer is preferably within a range of 0.1 to 10 mass%. By setting the amount of pigment in the chemical conversion treatment layer to 0.1 mass% or more, the black discoloration on the surface of the Zn-based plated layer can be made less noticeable. In addition, by setting the amount of pigment to 10 mass% or less, the metallic appearance of the Zn-based plated layer is not impaired. The amount of pigment is more preferably 0.1 to 5 mass% and still more preferably 0.1 to 3 mass% from the viewpoint of maintaining the metallic appearance.

10 [0043]

The amount of pigment in the chemical conversion treatment layer is measured through the following method. First, a thin film specimen of a chemical conversion treatment layer is prepared through a microtome method so that a cross section perpendicular to the rolling direction of the Zn-based plated steel sheet of the present embodiment can be observed. In a $20\ \mu\text{m} \times t\ \mu\text{m}$ region of the obtained thin film specimen (a region with $20\ \mu\text{m}$ in the direction parallel to the plate width direction and a thickness of $t\ \mu\text{m}$ in the plate thickness direction), a 200 kV field emission transmission electron microscope (FE-TEM) was used to observe at least 5 regions at a magnification of 100,000 times, and an energy dispersive X-ray analyzer (EDS or EDX) was used to perform elemental mapping. From the result of elemental mapping, the area proportion of the region where Cu, Co or Fe exists is obtained. Here, the area proportion of the region where Cu, Co, or Fe exists in a plurality of comparative samples having a chemical conversion treatment layer with a known pigment content is obtained through the same method as described above, and a calibration curve is prepared in advance from

the relationship with the amount of pigment. The amount of pigment of a target sample is obtained using the calibration curve.

[0044]

The pigment colors the chemical conversion treatment layer blue to make black
5 discoloration on the surface of the Zn-based plated layer less noticeable. However, if
the chemical conversion treatment layer contains a pigment, the corrosion resistance of
the chemical conversion treatment layer may deteriorate. Therefore, in order to prevent
deterioration of the corrosion resistance of the chemical conversion treatment layer, it is
preferable to optimize the mixing ratio between the silica particles and the pigment in the
10 chemical conversion treatment layer of the present embodiment. That is, it is preferable
that $[Si]/[Cu]$, $[Si]/[Co]$, or $[Si]/[Fe]$ be within a range of 1 to 200 as a mixing ratio
between the silica particles and the pigment in the chemical conversion treatment layer in
a case where an equivalent amount of Si in the silica particles is represented by $[Si]$ and
equivalent amounts of Cu, Co, and Fe in the pigment are respectively represented by
15 $[Cu]$, $[Co]$, and $[Fe]$. By setting $[Si]/[Cu]$, $[Si]/[Co]$, or $[Si]/[Fe]$ to 1 or more, the
corrosion resistance of the chemical conversion treatment layer can be improved even in
a case where the chemical conversion treatment layer contains a pigment. In addition,
by setting $[Si]/[Cu]$, $[Si]/[Co]$, or $[Si]/[Fe]$ to 200 or less, the deterioration of the
appearance of the Zn-based plated layer can be prevented. $[Si]/[Cu]$, $[Si]/[Co]$, or
20 $[Si]/[Fe]$ is more preferably 10 to 150 from the viewpoint of maintaining both the
corrosion resistance and the prevention of the deterioration of the appearance. In
addition, $[Si]/([Cu]+[Co]+[Fe])$ is more preferably within a range of 1 to 200 from the
viewpoint of making blue coloring of the chemical conversion treatment layer more
beautiful.

25 [0045]

The chemical conversion treatment layer may further contain either or both of a Nb compound and a phosphoric acid compound. In a case where the Nb compound and the phosphoric acid compound are incorporated, the corrosion resistance of the Zn-based plated layer is improved.

5 [0046]

As the Nb compound, conventionally known niobium-containing compounds can be used, and examples thereof include niobium oxide, niobic acid, and salts thereof, fluoroniobate, and fluorooxoniobate. Among these, niobium oxide is preferably used from the viewpoint of improving the corrosion resistance.

10 [0047]

Examples of phosphoric acid compounds include phosphoric acids such as orthophosphoric acid, metaphosphoric acid, pyrophosphoric acid, triphosphoric acid, and tetraphosphoric acid, and salts thereof; phosphonic acids such as aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), and salts thereof; and organic phosphoric acids such as phytic acid and salts thereof. Cationic species of salts are not particularly limited, and examples thereof include Cu, Co, Fe, Mn, Sn, V, Mg, Ba, Al, Ca, Sr, Nb, Y, Ni, and Zn. These may be used alone or in combination of two or more thereof.

20

[0048]

The Nb compound and the phosphoric acid compound are preferably contained in the chemical conversion treatment layer at a total rate of 0.5 to 30 mass%. If the amount of Nb compound or phosphoric acid compound is 0.5 mass% or more, the effect of improving corrosion resistance can be obtained, and if the amount of Nb compound or

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phosphoric acid compound is 30 mass% or less, the chemical conversion treatment layer does not become brittle and the Zn-based plated layer can be stably coated.

[0049]

The amount of Nb compound or phosphoric acid compound in the chemical conversion treatment layer is measured through the following method. First, a plurality of comparative samples having a chemical conversion treatment layer with a known Nb compound or phosphoric acid compound content are prepared separately from a target sample, surfaces thereof are measured with a fluorescent X-ray device, and a calibration curve is drawn from the relationship between the amount of Nb compound or phosphoric acid compound and the obtained detection intensity of Nb or P. Next, the target sample is measured with a fluorescent X-ray device under the same conditions as those of the comparative samples, and the amount of Nb compound or phosphoric acid compound is obtained using the above-described calibration curve from the obtained detection intensity of Si.

[0050]

Furthermore, the deposition amount of the chemical conversion treatment layer per surface of the Zn-based plated layer is 0.1 to 15 g/m². If the deposition amount of the chemical conversion treatment layer is 0.1 g/m² or more, the deposition amount is sufficient, the black discoloration on the surface of the Zn-based plated layer can be made less noticeable, and the corrosion resistance of the Zn-based plated layer can be improved. In addition, if the deposition amount is 15 g/m² or less, even if the chemical conversion treatment layer contains a pigment, the reflection of light on the surface of the chemical conversion treatment layer is reduced, and the metallic appearance of the surface of the Zn-based plated layer can be visually recognized. A more preferred deposition amount is 0.2 to 2 g/m².

[0051]

The chemical conversion treatment layer may further contain at least one cross-linking agent selected from the group consisting of a silane coupling agent, a cross-linking zirconium compound, and a cross-linking titanium compound. These may be used alone or in combination of two or more thereof.

[0052]

When the above-described at least one cross-linking agent selected from the group consisting of a silane coupling agent, a cross-linking zirconium compound, and a cross-linking titanium compound is incorporated, the adhesion between the Zn-based plated layer and the chemical conversion treatment layer is further improved.

[0053]

The above-described silane coupling agent is not particularly limited, and examples thereof include vinyltrimethoxysilane, vinyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropylethoxysilane, N-[2-(vinylbenzylamino)ethyl]-3-aminopropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldiethoxysilane, γ -methacryloxypropyltriethoxysilane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxypropylmethyldiethoxysilane, γ -glycidoxypropyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropylmethyldimethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, and γ -mercaptopropyltrimethoxysilane which are sold by Shin-Etsu Chemical Co., Ltd., Nippon Unicar Company Limited, Chisso

Corporation, Toshiba Silicone, and the like. The above-described silane coupling agent may be used alone or in combination of two or more thereof.

[0054]

The above-described cross-linking zirconium compound is not particularly limited as long as it is a zirconium-containing compound having a plurality of functional groups capable of reacting with a carboxyl group or a hydroxyl group, but is preferably a compound soluble in water or an organic solvent and more preferably a water-soluble zirconium compound. Examples of such compounds include zirconyl ammonium carbonate.

10 [0055]

The above-described cross-linking titanium compound is not particularly limited as long as it is a titanium-containing compound having a plurality of functional groups capable of reacting with a carboxyl group or a hydroxyl group, and examples thereof include dipropoxybis(triethanolamine)titanium, dipropoxybis(diethanolamine)titanium, propoxytris(diethanolamine)titanium, dibutoxybis(triethanolamine)titanium, dibutoxybis(diethanolamine)titanium, dipropoxybis(acetylacetonato)titanium, dibutoxybis(acetylacetonato)titanium, dihydroxybis(lactato)titanium monoammonium salt, dihydroxybis(lactato)titanium diammonium salt, propanedioxy titanium bis(ethylacetoacetate), oxotitanium bis(monoammonium oxalate), and isopropyltri(N-amidoethylaminoethyl) titanate. The above-described cross-linking agent may be used alone or in combination of two or more thereof.

[0056]

The above-described at least one cross-linking agent selected from the group consisting of a silane coupling agent, a cross-linking zirconium compound, and a cross-linking titanium compound is preferably incorporated in an amount of 0.1 to 50 mass%

based on 100 mass% of a solid content of the resin. In a case where the amount of this cross-linking agent is less than 0.1 mass%, the effect of improving adhesion may not be obtained. If the amount of the cross-linking agent exceeds 50 mass%, the stability of the aqueous composition may deteriorate.

5 [0057]

The chemical conversion treatment layer may further contain at least one cross-linking agent selected from the group consisting of an amino resin, a polyisocyanate compound, a block body thereof, an epoxy compound, and a carbodiimide compound. These cross-linking agents may be used alone or in combination of two or more thereof.

10 [0058]

In the case where the above-described at least one cross-linking agent selected from the group consisting of an amino resin, a polyisocyanate compound, a block body thereof, an epoxy compound, and a carbodiimide compound is incorporated, the cross-linking density increases, the barrier properties of the chemical conversion treatment layer are improved, and the corrosion resistance is further improved.

[0059]

The above-described amino resin is not particularly limited, and examples thereof include a melamine resin, a benzoguanamine resin, a urea resin, and a glycoluril resin.

20 [0060]

The above-described polyisocyanate compound is not particularly limited, and examples thereof include hexamethylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, and tolylene diisocyanate. In addition, a blocked product thereof is a blocked product of the above-described polyisocyanate compound.

25 [0061]

The above-described epoxy compound is not particularly limited as long as it is a compound having a plurality of oxirane rings, and examples thereof include adipic acid diglycidyl ester, phthalic acid diglycidyl ester, terephthalic acid diglycidyl ester, sorbitan polyglycidyl ether, pentaerythritol polyglycidyl ether, glycerin polyglycidyl ether, trimethylpropane polyglycidyl ether, neopentyl glycol polyglycidyl ether, ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 2,2-bis-(4'-glycidyloxyphenyl) propane, tris(2,3-epoxypropyl) isocyanurate, bisphenol A diglycidyl ether, hydrogenated bisphenol A diglycidyl ether.

10 [0062]

Examples of the above-described carbodiimide compound include compounds obtained by synthesizing isocyanate-terminated polycarbodiimide through a condensation reaction of diisocyanate compounds such as aromatic diisocyanate, aliphatic diisocyanate, and alicyclic diisocyanate which involves carbon dioxide removal and then adding a hydrophilic segment having a functional group having reactivity with a isocyanate group thereto.

[0063]

The above-described at least one cross-linking agent selected from the group consisting of an amino resin, a polyisocyanate compound, a block body thereof, an epoxy compound, and a carbodiimide compound is preferably incorporated in an amount of 0.1 to 50 mass% based on 100 mass% of a solid content of the resin. In a case where the amount of this cross-linking agent is less than 0.1 mass%, the effect of improving the corrosion resistance may not be obtained. If the amount of the cross-linking agent exceeds 50 mass%, the chemical conversion treatment layer may become brittle and the corrosion resistance may deteriorate.

[0064]

The chemical conversion treatment layer preferably further contains at least one selected from the group consisting of a vanadium compound, tungsten compound and a molybdenum compound. These may be used alone or in combination of two or more thereof.

[0065]

By incorporating the above-described at least one selected from the group consisting of a vanadium compound, tungsten compound and a molybdenum compound, the corrosion resistance of the chemical conversion treatment layer is improved.

[0066]

The above-described vanadium compound is not particularly limited. Conventionally known vanadium-containing compounds can be used, and examples thereof include vanadic acid, vanadates such as ammonium vanadate and sodium vanadate, phospho-vanadic acid, and phosphovanadates such as ammonium phosphovanadate.

[0067]

The above-described tungsten compound is not particularly limited. Conventionally known tungsten-containing compounds can be used, and examples thereof include tungstic acid, tungstates such as ammonium tungstate and sodium tungstate, phospho-tungstic acid, and phosphotungstates such as ammonium phosphotungstate.

[0068]

The above-described molybdenum compound is not particularly limited. Conventionally known molybdenum-containing compounds can be used, and examples thereof include molybdates. The above-described molybdates are not limited in its

skeleton and degree of condensation, and examples thereof include orthomolybdate, paramolybdate, and metamolybdate. In addition, all salts such as simple salts and double salts are included, and examples of double salts include molybdate phosphate.

[0069]

5 The above-described at least one selected from the group consisting of a vanadium compound, tungsten compound and a molybdenum compound is preferably incorporated in an amount of 0.01 to 20 mass% based on 100 mass% of a solid content of the resin. In a case where the amount of the above-described at least one selected from the group consisting of a vanadium compound, tungsten compound and a molybdenum
10 compound is less than 0.01 mass%, the effect of improving the corrosion resistance may not be obtained. In a case where the amount of the above-described at least one selected from the group consisting of a vanadium compound, tungsten compound and a molybdenum compound exceeds 20 mass%, the chemical conversion treatment layer may become brittle and the corrosion resistance may deteriorate.

15 [0070]

 The chemical conversion treatment layer may further contain a polyphenol compound.

[0071]

 By incorporating the above-described polyphenol compound, the corrosion
20 resistance of the chemical conversion treatment layer or adhesion of a post-coating film when used for post-coating applications or the like is improved.

[0072]

 The above-described polyphenol compound is a compound having two or more phenolic hydroxyl groups bound to a benzene ring, or a condensate thereof. Examples
25 of the above-described compound having two or more phenolic hydroxyl groups bound

to a benzene ring include gallic acid, pyrogallol, and catechol. The condensate of a compound having two or more phenolic hydroxyl groups bound to a benzene ring is not particularly limited, and examples thereof include a polyphenol compound which is commonly called tannic acid and widely distributed in the plant kingdom. Tannic acid is a general term for an aromatic compound which has a complex structure having a large number of phenolic hydroxyl groups and is widely distributed in the plant kingdom. The above-described tannic acid may be hydrolyzable tannic acid or condensed tannic acid. The above-described tannic acid is not particularly limited, and examples thereof include hamamelitannin, persimmon tannin, tea tannin, Chinese gall tannin, gallnut tannin, myrobalan tannin, dividivi tannin, algarovilla tannin, valonea tannin, and catechin tannin.

[0073]

As the above-described tannic acid, commercially available ones such as a “tannic acid extract A”, “B tannic acid”, “N tannic acid”, “industrial tannic acid”, “purified tannic acid”, “Hi tannic acid”, “F tannic acid”, and “JP tannic acid” (all are manufactured by Dainippon Pharmaceutical Co., Ltd.) and “tannic acid: AL” (manufactured by Fuji Chemical Industry Co., Ltd.) can be used, for example. The above-described polyphenol compound may be used alone or in a combination of two or more thereof.

[0074]

The above-described polyphenol compound is preferably incorporated in an amount of 0.1 to 50 mass% based on 100 mass% of a solid content of the resin. In a case where the amount of the above-described polyphenol compound is less than 0.1 mass%, the effect of improving corrosion resistance may not be obtained. If the amount

of the above-described polyphenol compound exceeds 50 mass%, the stability of the aqueous composition may deteriorate.

[0075]

The chemical conversion treatment layer may further contain a solid lubricant.

5 [0076]

Incorporating the above-described solid lubricant effectively improves lubricity of the chemical conversion treatment layer and processability during press forming, and prevents scratches due to molds, handling, or the like and abrasion scratches during transportation of molded products or coils.

10 [0077]

The above-described solid lubricant is not particularly limited, and examples thereof include well-known inorganic lubricants and lubricants based on fluorine, hydrocarbons, fatty acid amides, esters, alcohols, and metal soap. As a criterion for selecting a lubricating additive for improving the processability, it is necessary to select a substance that exists on the surface of the chemical conversion treatment layer rather than being dispersed in the chemical conversion treatment layer formed by an added lubricant from the viewpoints of reducing friction between a mold and the surface of a molded product and maximizing the lubrication effect. That is, in a case where the lubricant is dispersed in the formed chemical conversion treatment layer, the surface friction coefficient is high, the chemical conversion treatment layer is likely to be destroyed, and powdery substances are peeled off and accumulated, resulting in deterioration in processability and poor appearance called powdering phenomenon. As substances that are present on the surface of the chemical conversion treatment layer, ones which are incompatible with the resin and have a low surface energy are selected.

25 [0078]

Among these, use of polyolefin wax is more preferable because it lowers the coefficient of dynamic friction on the surface, greatly improves the processability, and improves the corrosion resistance after processing. Examples of this wax include hydrocarbon waxes such as paraffin, microcrystalline, and polyethylene. The melting points of the waxes are more preferably 70°C to 160°C because the film temperature increases due to deformation heat and friction heat of a material during processing. If the melting points of the waxes are lower than 70°C, they may soften and melt during processing, whereby excellent properties of the solid lubricant may not be exhibited. In addition, if the melting points of the waxes exceed 160°C, hard particles may be present on the surface of the waxes, which may reduce the frictional properties. Therefore, high forming processability may not be obtained.

[0079]

The particle diameters of these waxes are more preferably 0.1 to 5 μm . If the particle diameters of the waxes exceed 5 μm , distribution of solidified waxes may become uneven, or the waxes may fall off from the chemical conversion treatment layer. In addition, in a case where the particle diameters of the waxes are less than 0.1 μm , the processability may be insufficient.

[0080]

The above-described solid lubricant is preferably incorporated in an amount of 0.1 to 30 mass% based on 100 mass% of a solid content of the resin. In a case where the amount of the above-described solid lubricant is less than 0.1%, the effect of improving processability is small. If the amount of the above-described solid lubricant exceeds 30%, the corrosion resistance may deteriorate.

[0081]

The chemical conversion treatment layer is obtained by applying an aqueous composition containing components such as a resin, silica particles, blue organic pigments, Nb compounds, and phosphoric acid compounds to the surface of a Zn-based plated layer and drying it. A solvent may be used in the aqueous composition to improve film formability and form a more uniform and smooth film. The solvent is not particularly limited as long as it is commonly used in coating materials, and examples thereof include hydrophilic solvents based on alcohol, ketone, esters, and ethers from the viewpoint of leveling.

[0082]

The coating method of an aqueous composition used for forming a chemical conversion treatment layer is to apply the aqueous composition to the surface of a Zn-based plated layer to form a film. The coating method is not particularly limited, and generally used roll coating, air spraying, airless spraying, immersion, and the like can be employed as appropriate. In order to enhance curability of the chemical conversion treatment layer, it is preferable to heat an object to be coated in advance or heat-dry the object to be coated after coating. As a heat-drying method, any method such as hot air, induction heating, a near-infrared method, and a far-infrared method may be used, or the methods may be used in combination. The heating temperature of the object to be coated is 50°C to 250°C, preferably 70°C to 220°C. If the heating temperature is lower than 50°C, the evaporation rate of water is slow and sufficient film formability cannot be obtained, and therefore, the corrosion resistance may deteriorate. On the other hand, if the heating temperature exceeds 250°C, the resin is thermally decomposed, the corrosion resistance deteriorates, and the appearance deteriorates due to yellowing or the like. When heat-drying is performed after coating, the drying time is preferably 1 second to 5 minutes. In addition, if the resin is cured by electron beams or ultraviolet rays, it may

be cured by such irradiation, or the irradiation may be used in combination with heat-drying.

[0083]

In addition, it is preferable that an arithmetic average roughness Ra of the Zn-based plated layer be 0.5 to 2.0 μm and an arithmetic average height Sa of the chemical conversion treatment layer be 5 nm to 100 nm. When the arithmetic average roughness Ra of the Zn-based plated layer is 2.0 μm or less, the metallic appearance of the Zn-based plated layer can be maintained at a high level. When Ra exceeds 2.0 μm , the light applied to the surface of the Zn-based plated layer is likely to be diffusely reflected, and the metallic appearance is likely to deteriorate. When the arithmetic average height Sa of the chemical conversion treatment layer is 100 nm or lower, transparency of the chemical conversion treatment layer can be maintained. On the other hand, when Sa exceeds 100 nm, the light applied to the surface of the chemical conversion treatment layer is likely to be diffusely reflected, and the transparency of the chemical conversion treatment layer may decrease. When the arithmetic average roughness Ra of the Zn-based plated layer and the arithmetic average height Sa of the chemical conversion treatment layer are respectively less than or equal to the upper limits, the metallic appearance of the Zn-based plated layer can be maintained. In addition, even if the arithmetic average roughness Ra of the Zn-based plated layer and the arithmetic average height Sa of the chemical conversion treatment layer are respectively less than the lower limits, the effect of maintaining the metallic appearance or permeability is saturated. Therefore, they are respectively set to be greater than or equal to the lower limits. The arithmetic average roughness Ra of the Zn-based plated layer is measured and calculated with a 3D laser microscope (manufactured by Keyence Corporation). The height Z is measured at a measurement interval of 50 μm using a 20 $\times$ standard lens. The number of measurement

points is preferably 100 points. The number of measurement points is 100, and the obtained 100 points of the heights Z , heights Z_1 to Z_{100} , are used to calculate the arithmetic average roughness R_a from Equation 2 below. Z_{ave} is an average of the 100 points of the heights Z .

$$R_a = 1/100 \times \sum_{x=1 \rightarrow 100} (|Height Z_x - Z_{ave}|) \dots \text{Equation 2}$$

[0084]

The arithmetic average height S_a of the chemical conversion treatment layer is measured and calculated through the following method. The surface of a sample cut into a predetermined size from a Zn-based plated steel sheet is gold vapor-deposited to a thickness of 50 nm, the gold vapor-deposited sample is embedded in a resin, and the sample is polished so that the cross section in the plate thickness direction is exposed. The cross section of the sample is observed with a scanning electron microscope at a magnification of 5000 times, and the line roughness of the gold vapor-deposited layer when observed from a direction perpendicular to the cross section is calculated. The arithmetic average height S_a of the chemical conversion treatment layer is obtained by converting the obtained line roughness into a surface roughness difference. Gold vapor deposition is performed to clarify the boundary between the chemical conversion treatment layer and the resin, and the thickness of the gold vapor-deposited layer is negligible compared to that of the chemical conversion treatment layer. Therefore, the arithmetic average height of the gold vapor-deposited layer can be substituted for the arithmetic average height S_a of the surface of the chemical conversion treatment layer.

[0085]

The chemical conversion treatment layer is preferably formed on the surface of the Zn-based plated layer without using another film or the like. In addition, in order to

obtain a more beautiful metallic appearance, it is preferable that no other colored film, low-permeable film, or the like be provided on the chemically treated layer.

[0086]

Even if there is a chemical conversion treatment layer, from the viewpoint of reflecting the metallic appearance of the surface of the plated layer, when the Zn-based plated steel sheet of the present embodiment is measured with a multi-angle spectrophotometer, when L^* obtained when light is incident on the surface of the chemical conversion treatment layer at an angle of 60° from the surface of the chemical conversion treatment layer and the light reflected from the surface of the chemical conversion treatment layer is received at an angle of 135° from the surface of the chemical conversion treatment layer in a plane perpendicular to the surface of the chemical conversion treatment layer is defined as L^*_1 and L^* obtained when light is incident on the surface of the chemical conversion treatment layer at an angle of 120° from the surface of the chemical conversion treatment layer and the light reflected from the surface of the chemical conversion treatment layer is received at an angle of 135° from the surface of the chemical conversion treatment layer in the above-described plane is defined as L^*_2 , it is preferable that $L^*_1/L^*_2 \geq 2$ be satisfied. It has been found that this feature is an inherent property of a Zn-based plated steel sheet that has metallic luster even with a chemical conversion treatment layer and, as a result, has a metallic appearance. In addition to this range, by setting b^* in a case where evaluation is carried out in a CIE 1976 (L^* , a^* , b^*) color space to a range to be described below, a more beautiful metallic appearance can be maintained while making the blackening less noticeable. L^*_1/L^*_2 is more preferably 3 or more.

[0087]

[Appearance]

Next, the appearance of the Zn-based plated steel sheet of the present embodiment will be described. b^* in a case where an appearance of the Zn-based plated steel sheet of the present embodiment when viewed from the side of the chemical conversion treatment layer is evaluated in a CIE 1976 (L^* , a^* , b^*) color space is -30 to -2, a 60-degree mirror surface glossiness G_s (60°) specified in JIS Z 8741:1997 is 50 to 200, and the Zn-based plated steel sheet exhibits a metallic appearance. Hereinafter, the reason for limiting b^* and a 60-degree mirror surface glossiness G_s (60°) will be described.

10 [0088]

The more the light is reflected from the surface of the Zn-based plated layer, the higher the light brightness. If the light brightness is low, the reflection from the chemical conversion treatment layer increases. Therefore, if b^* is not a predetermined value, the metallic appearance of the Zn-based plated layer cannot be visually recognized. Therefore, it was found that predetermined 60-degree mirror surface glossiness G_s (60°) and b^* are preferably set to achieve excellent blackening resistance while allowing the metallic appearance of the Zn-based plated layer to be visually recognized. It is presumed that this is because the b^* -value fluctuates in the direction of increasing during blackening.

20 [0089]

If b^* is less than -30 in a case where evaluation is carried out in a CIE 1976 (L^* , a^* , b^*) color space, the blue color of the surface of the Zn-based plated steel sheet becomes darker, and the metallic appearance of the Zn-based plated layer is not visually recognized. In addition, if b^* exceeds -2, the blue color becomes pale, and the black discoloration on the surface of the Zn-based plated layer becomes noticeable, resulting in

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poor appearance. Accordingly, b^* is set to be within the range of -30 to -2. The lower limit value of b^* is preferably -22 and more preferably -15 from the viewpoint of maintaining the metallic appearance. The upper limit value of b^* is preferably -3.5 and more preferably -5 from the viewpoint of preventing blackening.

5 [0090]

In addition, as for the appearance of the Zn-based plated steel sheet of the present embodiment when viewed from the side of the chemical conversion treatment layer, L^* in a case where evaluation is carried out in a CIE 1976 (L^* , a^* , b^*) color space is preferably 85 or less. When L^* is 85 or less, there is an effect that the metallic appearance can be visually recognized more beautifully. From the viewpoint of making black discoloration less noticeable, L^* is more preferably 80 or less, and even more preferably 75 or less.

[0091]

In addition, when the 60-degree mirror surface glossiness G_s (60°) is less than 50, the appearance of the Zn-based plated steel sheet becomes almost white, and the metallic appearance of the Zn-based plated layer is not visually recognized. Further, when the 60-degree mirror surface glossiness G_s (60°) exceeds 200, the reflection from the surface of the chemical conversion treatment layer becomes strong, making it difficult to visually recognize the metallic appearance of the Zn-based plated layer. Here, the appearance in the present invention means an appearance of the Zn-based plated steel sheet when viewed from the side of the Zn-based plated layer placed on at least one surface of the steel sheet.

[0092]

In addition, a non-pattern portion and a pattern portion placed to have a predetermined shape may be formed on surface of the Zn-based plated layer according to the present embodiment.

It is preferable that the pattern portion be placed to have any one of a linear portion, a curved portion, a dot portion, figures, numerals, symbols, patterns, or characters, or a combined shape of two or more of these. Also, the non-pattern portion is a region other than the pattern portion. In addition, even if the shape of the pattern portion is partially missing, such as missing dots, it is permissible as long as it can be recognized as a whole. Also, the non-pattern portion may have a shape that borders the boundary of the pattern portion.

[0093]

When any one of a linear portion, a curved portion, a dot portion, figures, numerals, symbols, patterns, or characters, or a combined shape of two or more of these is placed on the surface of the Zn-based plated layer, these regions can be defined as the pattern portion, and the other regions can be defined as the non-pattern portion. The boundary between the pattern portion and the non-pattern portion can be recognized with the naked eye. The boundary between the pattern portion and the non-pattern portion may be grasped from an enlarged image using an optical microscope, a magnifying glass, or the like.

[0094]

The pattern portion is preferably formed in a size to a degree in which the presence of the pattern portion can be determined with the naked eye or under a magnifying glass or a microscope. In addition, the non-pattern portion is a region that occupies most of the Zn-based plated layer (the surface of the Zn-based plated layer), and the pattern portion may be placed in the non-pattern portion.

The pattern portion is placed to have a predetermined shape in the non-pattern portion. Specifically, the pattern portion is placed to have any one of a linear portion, a curved portion, figures, a dot portion, figures, numerals, symbols, patterns, or characters, or a combined shape of two or more of these in the non-pattern portion. By adjusting the shape of the pattern portion, any one of a linear portion, a curved portion, figures, a dot portion, figures, numerals, symbols, patterns, or characters, or a combined shape of two or more of these appears on the Zn-based plated layer. For example, character strings, numeric strings, symbols, marks, diagrams, design images, or a combination thereof consisting of the pattern portion appear on the surface of the Zn-based plated layer. Such shapes are shapes intentionally or artificially formed through a production method to be described below, and are not naturally formed.

[0095]

In this manner, the pattern portion and the non-pattern portion are regions formed on the surface of the Zn-based plated layer and each contain one or two of a first region and a second region.

[0096]

The pattern portion and the non-pattern portion each contain one or two of a first region and a second region determined by any of determination methods 1 to 5 below, and an absolute value of the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion is 30% or more. In the case where the absolute value of the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion is 30% or more, the pattern portion and the non-pattern portion can be distinguished. If the difference between the area proportions is less than 30%, the difference between the area proportion of the first region in the pattern portion

and the area proportion of the first region in the non-pattern portion is small, and the appearances of the pattern portion and the non-pattern portion look similar, whereby it is difficult to distinguish the pattern portion. The larger the difference between the area proportions, the better. The difference between the area proportions is more preferably 5 40% or more and more preferably 60% or more.

[0097]

That is, in the pattern portion, the area proportions of the first region and the second region can be obtained. In a case where the area fraction of the first region exceeds 70%, the pattern portion relatively appears white or almost white compared to a 10 case where the area fraction of the first region is 70% or less. In a case where the area fraction of the first region is 30% to 70%, the pattern portion appears to have a relatively pear skin-like look. In addition, in a case where the area fraction of the first region is less than 30%, the pattern portion appears to have relatively metallic luster. In this manner, the appearance of the pattern portion depends on the area fraction of the first 15 region.

[0098]

On the other hand, also in the non-pattern portion, the area proportions of the first region and the second region can be obtained. Similarly to the pattern portion, the appearance of the non-pattern portion depends on the area fraction of the first region.

20 [0099]

In the case where the absolute value of the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion is 30% or more, the pattern portion and the non-pattern portion can be distinguished. If the difference between the area proportions is less than 25 30%, the difference between the area proportion of the first region in the pattern portion

and the area proportion of the first region in the non-pattern portion is small, and the appearances of the pattern portion and the non-pattern portion look similar, whereby it is difficult to distinguish the pattern portion. The larger the difference between the area proportions, the better. The difference between the area proportions is more preferably 40% or more and more preferably 60% or more.

[0100]

[Determination method 1]

In a determination method 1, virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region partitioned by the virtual grid lines is defined as a measurement region A, and an L^* -value in each measurement region A is measured.

When arbitrary 50 points are selected from the obtained L^* -values and an average of the obtained L^* -values at the 50 points is defined as a standard L^* -value, a region in which the L^* -value is equal to or more than the standard L^* -value is defined as a first region and a region in which the L^* -value is less than the standard L^* -value is defined as a second region.

[0101]

[Determination method 2]

In a determination method 2, virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region partitioned by the virtual grid lines is defined as a measurement region A, an L^* -value in each measurement region A is measured, a region in which the L^* -value is 45 or more is defined as a first region, and a region in which the L^* -value is less than 45 is defined as a second region.

[0102]

[Determination method 3]

In a determination method 3, virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, and an arithmetic average height Sa2 is measured in each of a plurality of regions partitioned by the virtual grid lines. A region in which the obtained arithmetic average height Sa2 is 1 μm or more is defined as a first region, and a region in which the obtained arithmetic average height Sa2 is less than 1 μm is defined as a second region. The arithmetic average height Sa2 is measured using a 3D laser microscope (manufactured by Keyence Corporation). In the present embodiment, a 20× standard lens is used to measure the height Z in each of a plurality of regions partitioned by virtual grid lines at measurement intervals of 50 μm. In a case where the measurement is performed on the grids, 100 measurement points are obtained in the regions. The obtained 100 points of the heights Z, heights Z1 to Z100, are used to calculate the arithmetic average height Sa2 from Equation 3 below. Zave is an average of the 100 points of the heights Z.

$$Sa2 = 1/100 \times \sum_{x=1 \rightarrow 100} (|Height Zx - Zave|) \dots \text{Equation 3}$$

[0103]

[Determination method 4]

In determination method 4, virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a plane (0002) of a Zn phase and a diffraction peak intensity I_{10-11} of a plane (10-11) of the Zn phase are measured for each region through an X-ray diffraction method in which X-rays are respectively made to be incident on the plurality of regions partitioned by the virtual grid lines, and a proportion of these intensities (I_{0002}/I_{10-11}) is defined as an orientation rate. A region in which the orientation rate is 3.5 or more is defined as a

first region, and a region in which the orientation rate is less than 3.5 is defined as a second region.

[0104]

[Determination method 5]

5 In a determination method 5, virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm, and a circle S centered at a centroid point G of each region is drawn for each of a plurality of regions partitioned by the virtual grid lines. A diameter R of the circle S is set so that a total length of surface boundary lines of the Zn-based plated layer contained in the circle S is 10 mm. An average value of a
10 maximum diameter R_{max} and a minimum diameter R_{min} among diameters R of circles S in the plurality of regions is defined as a standard diameter R_{ave}, a region having a circle S of which the diameter R is less than the standard diameter R_{ave} is defined as a first region, and a region having a circle S of which the diameter R is greater than or equal to the standard diameter R_{ave} is defined as a second region.

15 [0105]

 The pattern portion and the non-pattern portion in which the first regions and the second regions are specified by the determination method 1 or 2 are formed after the formation of the Zn-based plated layer. The pattern portion and the non-pattern portion are formed by attaching an acidic solution to the surface of the Zn-based plated layer at
20 60°C to 200°C. More specifically, it is preferable that an acidic solution be prepared and attached to the surface of the Zn-based plated layer by printing means. As the printing means, general printing methods such as an ink jet method and printing methods (such as gravure printing, flexographic printing, offset printing, or silk printing) in which various plates are used can be applied.

25 [0106]

At a site where the acidic solution adheres, the very surface of the Zn-based plated layer dissolves, and the surface of the Zn-based plated layer changes from a state being plated. Accordingly, the appearance of the site where the acidic solution adheres changes as compared with a site to which the acidic solution does not adhere. In this manner, it is assumed that the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion becomes large, whereby the pattern portion and the non-pattern portion can be distinguished.

[0107]

The range in which the acidic solution adheres may be a region corresponding to the pattern portion or a region corresponding to the non-pattern portion.

[0108]

As the acidic solution, inorganic acids such as hydrochloric acid, nitric acid, and sulfuric acid are preferably used. In addition, the concentration of the acid in the acidic solution is desirably 0.1 to 10 mass%. The temperature of the steel sheet when the acidic solution adheres is 60°C to 200°C, desirably 50°C to 80°C. By adjusting the type and concentration of the acidic solution, it is possible to adjust the area fractions of the first region and the second region on the surface of the Zn-based plated layer at the site where the acidic solution adheres.

[0109]

If the surface temperature of the Zn-based plated layer when the acidic solution is attached is lower than 60°C, it takes time to form the pattern portion or the non-pattern portion, which is not preferable. If the surface temperature of the Zn-based plated layer exceeds 200°C, the acidic solution quickly evaporates, making it impossible to form the pattern portion or the non-pattern portion, which is not preferable.

[0110]

After adhesion of the acidic solution, it is necessary to wash with water within 1 to 10 seconds.

[0111]

5 Next, the pattern portion and the non-pattern portion in which the first regions and the second regions are specified by the determination method 3 are formed after the formation of the Zn-based plated layer. The pattern portion and the non-pattern portion are formed by pressing a roll having partially increased surface roughness against the surface of the Zn-based plated layer and transferring the surface shape of the roll to the
10 Zn-based plated layer. For example, in order to form a pattern portion on the surface of a Zn-based plated layer, the roughness of a site of the roll surface corresponding to the pattern portion can be made larger than that of the other sites to form a pattern portion including a large area of the first region having large surface roughness. Conversely, a roll in which the roughness of the site corresponding to the pattern portion is made
15 smaller than that of the other site may be used. Regarding the roughness of the roll surface (arithmetic average height Sa_2 (μm)), the range of roughness at the site where the roughness is increased is 0.6 to 3.0 μm and preferably 1.2 to 3.0 μm . The range of the roughness at the site where the roughness is lowered is preferably 0.05 to 1.0 μm and more preferably 0.05 to 0.8 μm . The transfer is preferably performed when the surface
20 temperature of the Zn-based plated layer is within a range of 100°C to 300°C. In addition, the difference between the roughness at the site having increased roughness and the roughness at the site having decreased roughness is set to be greater than 0.2 μm , preferably 0.3 μm or more in terms of the arithmetic average height Sa_2 . If the

difference in roughness decreases, it is difficult to distinguish between the pattern portion and the non-pattern portion.

[0112]

The pattern portion and the non-pattern portion specified through the
5 determination method 4 are formed by locally blowing a non-oxidizing gas to a molten metal using a gas nozzle on the steel sheet immediately after being pulled out of a hot-dip plating bath. Nitrogen or argon may be used as the non-oxidizing gas. Although the optimum temperature range differs depending on the composition, it is preferable to blow the non-oxidizing gas when the temperature of the molten metal is within a range of
10 (final solidification temperature -5)°C to (final solidification temperature +5)°C.

Furthermore, the temperature of the non-oxidizing gas is set to be lower than the final solidification temperature.

[0113]

When the temperature of the Zn-based plated layer is within the above-described
15 temperature range, the cooling rate of the molten metal increases at a site where the non-oxidizing gas is blown, thereby increasing the orientation rate of the Zn-based plated layer after solidification. On the other hand, the cooling rate of the molten metal is lowered at a site where the non-oxidizing gas is not blown, thereby lowering the orientation rate of the Zn-based plated layer after solidification. Accordingly, by
20 adjusting the blowing range of the non-oxidizing gas, it is possible to intentionally or arbitrarily adjust the sites where the region with a high orientation rate and the region with a low orientation rate appear.

[0114]

Accordingly, the shapes of the pattern portion and the non-pattern portion can be
25 arbitrarily adjusted, and the pattern portion and the non-pattern portion can be

distinguished. The lower the temperature of the gas blown, the higher the orientation rate. Therefore, the orientation rate can be adjusted by the temperature of the gas blown. The gas temperature is preferably lower than the final solidification temperature. For example, the gas temperature may be adjusted to 25°C to 250°C.

5 [0115]

The pattern portion and the non-pattern portion specified through the determination method 5 are formed by locally blowing a non-oxidizing gas having a final solidification temperature of the plating or higher to a molten metal using a gas nozzle on the steel sheet immediately after being pulled out of a hot-dip plating bath. Nitrogen or
10 argon may be used as the non-oxidizing gas. Although the optimum temperature range differs depending on the composition, it is preferable to blow the non-oxidizing gas when the temperature of the molten metal is within a range of (final solidification temperature - 5)°C to (final solidification temperature +5)°C. Furthermore, the temperature of the non-oxidizing gas is preferably set to be higher than or equal to the final solidification
15 temperature. For example, in the plating composition of Al: 11% and Mg: 3%, the non-oxidizing gas having a gas temperature at a final solidification temperature or higher is preferably blown when the temperature of the molten metal is 330°C to 340°C.

[0116]

The cooling rate of the molten metal decreases in the periphery where the non-oxidizing gas is blown. Accordingly, the boundaries or grain boundaries appearing on
20 the surface become coarse. Accordingly, by adjusting the range and amount of blowing the non-oxidizing gas, the size of the boundaries or grain boundaries appearing on the surface can be arbitrarily adjusted.

[0117]

By setting the absolute value of the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion to 30% or more, the pattern portion and the non-pattern portion can be distinguished. The formed pattern portion and non-pattern portion are not formed by printing or coating, and therefore have high durability. In addition, since the pattern portion and non-pattern portion are not formed by printing or coating, there is no influence on the corrosion resistance of the Zn-based plated layer. Accordingly, the Zn-based plated steel sheet of the present embodiment has excellent corrosion resistance.

[0118]

In the Zn-based plated layer in which the pattern portion is formed, a Zn-based plated steel sheet having high durability of the pattern portion and suitable plating properties such as corrosion resistance can be provided. Since the pattern portion can be intentionally or artificially formed, it can be placed to have any one of a linear portion, a curved portion, a dot portion, figures, numerals, symbols, patterns, or characters, or a combined shape of two or more of these. Accordingly, various designs, trademarks, and other identification marks can be displayed on the surface of the Zn-based plated layer without printing or coating, and the identification properties of the origin of the steel sheet, design properties of the steel sheet, and the like can be improved. In addition, information necessary for process management, inventory management, and the like or arbitrary information requested by consumers can also be provided to a hot-dip plated steel sheet using the pattern portion. This can also contribute to improving the productivity of the Zn-based plated steel sheet.

[0119]

According to the Zn-based plated steel sheet of the present embodiment, a chemical conversion treatment layer containing a pigment is formed on the Zn-based

plated layer in which the pattern portion is formed, so that the visibility of the pattern portion can be further improved.

[Examples]

[0120]

5 Hereinafter, the present invention will be specifically described using examples.

[0121]

First, a cold-rolled steel sheet with a thickness of 1 mm was prepared and immersed in a plating bath of each composition, and the plating deposition amount was adjusted to 80 g/m² per surface by N₂ wiping. The plating composition of the Zn-based
10 plated steel sheet obtained is shown in Table 1.

[0122]

In addition, in a case where a pattern portion is formed on the Zn-based plated layer, a pattern was formed through the following method. The pattern portion and the non-pattern portion each contained one or two of a first region and a second region
15 determined by any method of the determination methods 1 to 5, and an absolute value of the difference between the area proportion of the first region in the pattern portion and the area proportion of the first region in the non-pattern portion was 40%.

[0123]

<Pattern 1>

20 A hydrochloric acid solution was attached to a rubber plate having a convex portion or a concave portion with a square pattern with a side of 50 mm, and this rubber plate was pressed against the surface of a Zn-based plated layer to attach the acidic solution to a steel sheet, thereby forming a square pattern portion. The surface temperature of the Zn-based plated layer of the hot-dip plated steel sheet during the
25 attachment of the acidic solution was set to be within a range of 60°C to 200°C. In

addition, a portion other than the square pattern portion was defined as a non-pattern portion. Based on determination method 2, virtual grid lines were drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region partitioned by the virtual grid lines was defined as a measurement region A, an L^* -value in each measurement region A was measured, a region in which the L^* -value was 45 or more was defined as a first region, and a region in which the L^* -value was less than 45 was defined as a second region. This Zn-based plated steel sheet was set to Example 70.

[0124]

10 <Pattern 2>

With the surface temperature of a Zn-based plated layer set to 100°C to 300°C, a pattern portion was formed by pressing a roll having a square pattern with a side of 50 mm against the surface of the Zn-based plated layer. The square pattern portion was defined as a pattern portion, and the portion other than the square pattern was defined as a non-pattern portion. Based on determination method 3, virtual grid lines were drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, and an arithmetic average height Sa2 was measured in each of a plurality of regions partitioned by the virtual grid lines. A region in which the obtained arithmetic average height Sa2 was 1 μm or more was defined as a first region, and a region in which the obtained arithmetic average height Sa2 was less than 1 μm was defined as a second region. This Zn-based plated steel sheet was set to Example 71.

[0125]

<Pattern 3>

Nitrogen gas which is a type of non-oxidizing gas was blown to molten metal on the surface of a steel sheet using a gas nozzle when the temperature of the molten metal

was within a range of (final solidification temperature -5)°C to (final solidification temperature +5)°C when the steel sheet was pulled out of a plating bath. The gas temperature was lower than the final solidification temperature. Thereafter, the molten metal was completely solidified by cooling. The blowing range of the nitrogen gas was controlled to form a square pattern with a side of 50 mm. The square pattern portion was defined as a pattern portion, and the portion other than the square pattern was defined as a non-pattern portion. Based on the determination method 4, virtual grid lines were drawn on a surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a plane (0002) of a Zn phase and a diffraction peak intensity I_{10-11} of a plane (10-11) of the Zn phase were measured for each region through an X-ray diffraction method in which X-rays were respectively made to be incident on the plurality of regions partitioned by the virtual grid lines, and a proportion of these intensities (I_{0002}/I_{10-11}) was defined as an orientation rate. A region in which the orientation rate was 3.5 or more was defined as a first region, and a region in which the orientation rate was less than 3.5 was defined as a second region. This Zn-based plated steel sheet was set to Example 72.

[0126]

<Pattern 4>

Heated nitrogen gas which is a type of non-oxidizing gas was blown to molten metal on the surface of a steel sheet from a gas nozzle when the temperature of the molten metal was within a range of (final solidification temperature -5)°C to (final solidification temperature +5)°C when the steel sheet was pulled out of a plating bath. The conditions for blowing nitrogen gas are as shown in Table 1. The gas temperature was higher than or equal to the final solidification temperature. Thereafter, the molten

metal was completely solidified by cooling. The blowing range of the nitrogen gas was controlled to form a square pattern with a side of 50 mm. The square pattern portion was defined as a pattern portion, and the portion other than the square pattern was defined as a non-pattern portion. Based on the determination method 5, virtual grid lines were drawn on a surface of the Zn-based plated layer at intervals of 1 mm, and a circle S centered at a centroid point G of each region was drawn for each of a plurality of regions partitioned by the virtual grid lines. A diameter R of the circle S was set so that a total length of surface boundary lines of the Zn-based plated layer contained in the circle S was 10 mm. An average value of a maximum diameter $R_{\max}$ and a minimum diameter $R_{\min}$ among diameters R of circles S in the plurality of regions was defined as a standard diameter R_{ave} , a region having a circle S of which the diameter R was less than the standard diameter R_{ave} was defined as a first region, and a region having a circle S of which the diameter R was greater than or equal to the standard diameter R_{ave} was defined as a second region. This Zn-based plated steel sheet was set to Example 73 and 74.

[0127]

Next, if necessary, the Zn-based plated steel sheet was immersed in a Co sulfate solution, a Fe sulfate solution, or a Ni sulfate solution to precipitate 1 mg/m² of Co, Fe, or Ni on the surface of the Zn-based plated layer. The configuration of the Zn-plated layer is shown in Tables 3A and 3B.

[0128]

The arithmetic average roughness R_a of the Zn-based plated layer was measured with a 3D laser microscope (manufactured by Keyence Corporation). In the present example, a 20× standard lens was used to measure the height Z in each of a plurality of regions partitioned by virtual grid lines at measurement intervals of 50 μm. The

measurement was performed on the grids, and 100 measurement points were obtained in the regions. The obtained 100 points of the heights Z were set to heights Z_1 to Z_{100} , and the arithmetic average roughness R_a was calculated using Equation 2 above. Z_{ave} is an average of the 100 points of the heights Z .

5 [0129]

Next, an aqueous composition containing various aqueous resins (a urethane resin, a polyester resin, a polyolefin resin, an epoxy resin, an acrylic resin, a phenol resin, and a fluorine resin), silica particles, niobium oxide, sodium phosphate, and various pigments (copper sulfate, cobalt sulfate, iron sulfate, Cu-phthalocyanine (copper (II) phthalocyanine), Co-phthalocyanine (cobalt (II) phthalocyanine), iron oxide, carbon black, quinacridone red, bismuth vanadium, and titanium oxide) was applied to the surface of the Zn-based plated layer of the produced Zn-based plated steel sheet with a bar coater so that the dry deposition amount becomes 1.5 g/m^2 , dried at a reached sheet temperature of 150°C in a hot air drying furnace, and then water-cooled to form a

10 chromate-free chemical conversion treatment layer. The amounts of niobium oxide and sodium phosphate were each set to 5%. The details of the pigments are shown in Table 2A. In addition, the details of the silica particles are shown in Table 2B.

15 [0130]

The compositions and the like of chemical conversion treatment layers are shown in Tables 4A to 5B. In the "20% or more" column of Tables 4A and 4B, in a case where the amount of resin in a chemical conversion treatment layer was 20% or more, it was scored "○ (good)", and in a case where the amount of resin in a chemical conversion treatment layer was less than 20%, it was scored "× (bad)". In addition, in the "Nb-oxide" column of Tables 5A and 5B, in a case where niobium oxide was incorporated, it

20 was scored "○ (good)", and in a case where niobium oxide was not incorporated, it was

25

scored “× (bad)”. In addition, in the “Na-phosphate” column, in a case where sodium phosphate was incorporated, it was scored “○ (good)”, and in a case where sodium phosphate was not incorporated, it was scored “× (bad)”. In addition, in Comparative Examples 5 and 6, the drying temperature was set out of a range of 50°C to 250°C and
5 the drying time was set out of a range of 1 second to 5 minutes.

[0131]

(Arithmetic average height of chemical conversion treatment layer)

The arithmetic average height Sa of the chemical conversion treatment layer was obtained through the following method. The surface of a sample cut into a
10 predetermined size from a Zn-based plated steel sheet was gold vapor-deposited to a thickness of 50 nm, the gold vapor-deposited sample was embedded in a resin, and the sample was polished so that the cross section in the plate thickness direction was exposed. The cross section of the sample was observed with a scanning electron microscope at a magnification of 5000 times, and the roughness of the gold vapor-
15 deposited layer when observed from a direction perpendicular to the cross section was calculated to obtain the arithmetic average height Sa of the chemical conversion treatment layer. The gold vapor deposition was carried out to clarify the boundary between the chemical conversion treatment layer and the resin. Since the thickness of the gold vapor-deposited layer was negligible compared to that of the chemical
20 conversion treatment layer, the arithmetic average height of the gold vapor-deposited layer was substituted for the arithmetic average height Sa of the surface of the chemical conversion treatment layer.

[0132]

(60-Degree mirror surface glossiness G_s (60°))

A glossmeter (UGV-6P manufactured by Suga Test Instruments Co., Ltd.) was used to measure the 60° glossiness (%) of the surface of a Zn-plated layer based on a method JIS Z 8741. In a case where the glossiness was 50% to 200%, it was scored “A”, and in a case where the glossiness was less than 50%, it was scored “B”. The results are shown in Tables 5A and 5B.

[0133]

(b* -value)

A spectrophotometer (SE6000 manufactured by NIPPON Denshoku industries Co., Ltd.) was used to measure the surface of the Zn-plated layer. In a case where b* was -15 to -5, it was scored “AAA”, in a case where b* was -22 to -3.5 (excluding -15 to -5), it was scored “AA”, in a case where b* was -30 to -2 (excluding -22 to -3.5), it was scored “A”, and in a case where b* was greater than -2 and less than -30, it was scored “B”. The results are shown in Tables 5A and 5B.

[0134]

15 (L* -value)

A spectrophotometer (SE6000 manufactured by Denshoku industries Co., Ltd.) was used to measure L*. In a case where L* was 75 or less, it was scored “AAA”, in a case where L* was greater than 75 and less than or equal to 80, it was scored “AA”, in a case where L* was greater than 80 and less than or equal to 85, it was scored “A”, and in a case where L* was greater than 85, it was scored “B”. The results are shown in Tables 5A and 5B.

[0135]

(Metallic luster feeling)

A multi-angle spectrophotometer (MA T12 manufactured by X-Rite Inc.) was used to evaluate the metallic luster feeling. When L* obtained when light was incident

on the surface of the chemical conversion treatment layer at an angle of 60° from the surface of the chemical conversion treatment layer and the light reflected from the surface of the chemical conversion treatment layer was received at an angle of 135° from the surface of the chemical conversion treatment layer in a plane perpendicular to the surface of the chemical conversion treatment layer was defined as L^*_1 and L^* obtained when light was incident on the surface of the chemical conversion treatment layer at an angle of 120° from the surface of the chemical conversion treatment layer and the light reflected from the surface of the chemical conversion treatment layer was received at an angle of 135° from the surface of the chemical conversion treatment layer in the above-described plane was defined as L^*_2 , in a case where L^*_1/L^*_2 was 3 or more, it was scored “AA”, in a case where L^*_1/L^*_2 was greater than or equal to 2 and less than 3, it was scored “A”, and in a case where L^*_1/L^*_2 was less than 2, it was scored “B”. The results are shown in Tables 5A and 5B.

[0136]

15 (Blackening resistance)

Blackening resistance was evaluated by color difference ΔE^*_{ab} based on a color change of the surface of a Zn-plated layer before and after a test when a Zn-based plated steel sheet was allowed to stand under high temperature and high humidity conditions of 70°C and 80 %RH for 12 days. The color difference is represented by Equation 4 below when a chromaticness indices in the $L^*a^*b^*$ color system are a^* and b^* and a lightness index is L^* .

[0137]

$$\Delta E^*_{ab} = \sqrt{((\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2)} \dots \text{Equation 4}$$

[0138]

However, in the above-described equation, Δa^* is a difference between a^* of the Zn-based plated layer before the test and a^* of the Zn-based plated layer after the test, and Δb^* is a difference between b^* of the Zn-based plated layer before the test and b^* of the Zn-based plated layer after the test, and ΔL^* is a difference between L^* of the Zn-based plated layer before the test and L^* of the Zn-based plated layer after the test. The evaluation was determined according to the scores shown below, and scores of 4 and 3 were considered acceptable. The results are shown in Tables 6A and 6B.

[0139]

4: $\Delta E^*_{ab} \leq 5$

10 3: $5 < \Delta E^*_{ab} \leq 10$

2: $10 < \Delta E < \Delta E^*_{ab} \leq 15$

1: $\Delta E^*_{ab} > 15$

[0140]

(Corrosion resistance)

15 A salt spray test (JIS Z 2371:2015) was performed on a Zn-based plated steel sheet. The occurrence of white rust on a portion subjected to Erichsen processing after 120 hours of the test time was observed and determined according to the scores shown below. Among the scores, 3 or more was regarded as acceptable. The results are shown in Tables 6A and 6B.

20 [0141]

4: Less than 5% of occurrence of white rust

3: Greater than or equal to 5% and less than 10% of occurrence of white rust

2: Greater than or equal to 10% and less than 30% of occurrence of white rust

1: Greater than or equal to 30% of occurrence of white rust

[0142]

(Metallic appearance)

When the surface of a Zn-plated layer of a Zn-based plated steel sheet was shown to 5 panelists, the metallic appearance of plating was determined in a way it is seen. The evaluation was determined according to the scores shown below, and scores of 4 and 3 were considered acceptable. The results are shown in Tables 6A and 6B.

[0143]

4: 4 or more out of 5 panelists could visually recognize the metallic appearance of plating.

10 3: 3 out of 5 panelists could visually recognize the metallic appearance of plating.

2: 2 out of 5 panelists could visually recognize the metallic appearance of plating.

15 1: 1 out of 5 panelists could visually recognize the metallic appearance of plating.

[0144]

(Weather Resistance)

After testing the surface of a Zn-plated layer of a Zn-based plated steel sheet with a sunshine weather meter tester for 500 hours, the evaluation of a chemical conversion treatment layer was determined from the ratio of a initial film thickness to the thickness after the test according to the scores shown below, and scores 4 and 3 were considered acceptable. The results are shown in Tables 6A and 6B.

[0145]

25 4: The remaining proportion of the chemical conversion treatment layer is 90% or more.

3: The remaining proportion of the chemical conversion treatment layer is greater than or equal to 50% and less than 90%.

2: The remaining proportion of the chemical conversion treatment layer is greater than or equal to 30% and less than 50%.

5 1: The remaining proportion of the chemical conversion treatment layer is less than 30%.

[0146]

[Table 1]

	Average composition (mass%) of plated layer with balance being Zn and impurities					
	Al	Mg	Si	Sb	Pb	Ni
Plated layer 1	0.05	-	-	-	-	-
Plated layer 2	6	-	-	-	-	-
Plated layer 3	11	-	-	-	-	-
Plated layer 4	20	-	-	-	-	-
Plated layer 5	55	-	-	-	-	-
Plated layer 6	60	-	-	-	-	-
Plated layer 7	3	3	-	-	-	-
Plated layer 8	4	3	-	-	-	-
Plated layer 9	6	3	-	-	-	-
Plated layer 10	11	3	-	-	-	-
Plated layer 11	22	3	-	-	-	-
Plated layer 12	23	3	-	-	-	-
Plated layer 13	11	1	-	-	-	-
Plated layer 14	11	5	-	-	-	-
Plated layer 15	11	10	-	-	-	-
Plated layer 16	11	11	-	-	-	-
Plated layer 17	11	3	0.01	-	-	-
Plated layer 18	11	3	0.2	-	-	-
Plated layer 19	11	3	1	-	-	-
Plated layer 20	11	3	2	-	-	-
Plated layer 21	6	3	0.01	-	-	-
Plated layer 22	6	3	0.1	-	-	-
Plated layer 23	6	3	1	-	-	-
Plated layer 24	6	3	2	-	-	-
Plated layer 25	0.1	-	-	0.08	-	-
Plated layer 26	0.1	-	-	-	0.08	-
Plated layer 27	0.1	-	-	-	-	0.08
Plated layer 28	11	3	0.0001	-	-	-
Plated layer 29	11	3	-	0.0001	-	-
Plated layer 30	11	3	-	2	-	-
Plated layer 31	11	3	-	-	0.0001	-
Plated layer 32	11	3	-	-	2	-
Plated layer 33	11	3	-	-	-	0.0001
Plated layer 34	11	3	-	-	-	2

[0147]

5 [Table 2A]

Pigments	Details
Cu-phthalocyanine	AF Blue E-2B manufactured by Dainippon Pharmaceutical Co., Ltd.
Co-phthalocyanine	PB-75 manufactured by Dainippon Pharmaceutical Co., Ltd.
Iron oxide	Reagent manufactured by Kanto Chemical Co., Inc.
Copper oxide	Reagent manufactured by Kanto Chemical Co., Inc.
Cobalt sulfate	Reagent manufactured by Kanto Chemical Co., Inc.
Iron sulfate	Reagent manufactured by Kanto Chemical Co., Inc.

[0148]

[Table 2B]

	Details	Average particle diameter (nm)
Silica	ST-X5 manufactured by Nissan Chemical Corporation	5
Silica	ST-S manufactured by Nissan Chemical Corporation	9
Silica	ST-30L manufactured by Nissan Chemical Corporation	45
Silica	MP-1040 manufactured by Nissan Chemical Corporation	100
Silica	MP-2040 manufactured by Nissan Chemical Corporation	200
Silica	MP-4540M manufactured by Nissan Chemical Corporation	450

[0149]

[Table 3A]

	Zn-based plated layer			
	Type of plated layer	Pattern	Metal on surface of plated layer	Arithmetic average roughness Ra (μm)
Example 1	Plated layer 18	None	Co	0.8
Example 2	Plated layer 18	None	Co	0.8
Example 3	Plated layer 18	None	Co	0.8
Example 4	Plated layer 18	None	Co	0.8
Example 5	Plated layer 18	None	Co	0.8
Example 6	Plated layer 18	None	Co	0.8
Example 7	Plated layer 18	None	Co	0.8
Example 8	Plated layer 18	None	Co	0.8
Example 9	Plated layer 18	None	Co	0.8
Example 10	Plated layer 18	None	Co	0.8
Example 11	Plated layer 18	None	Co	0.8
Example 12	Plated layer 18	None	Co	0.8
Example 13	Plated layer 18	None	Co	0.8
Example 14	Plated layer 18	None	Co	0.8
Example 15	Plated layer 18	None	Co	0.8
Example 16	Plated layer 18	None	Co	0.8
Example 17	Plated layer 18	None	Co	0.8
Example 18	Plated layer 18	None	Co	0.8
Example 19	Plated layer 18	None	Co	0.8
Example 20	Plated layer 18	None	Co	0.8
Example 21	Plated layer 18	None	Co	0.8
Example 22	Plated layer 18	None	Co	0.8
Example 23	Plated layer 18	None	Co	0.8
Example 24	Plated layer 18	None	Co	0.5
Example 25	Plated layer 18	None	Co	2
Example 26	Plated layer 18	None	Co	2.5
Example 27	Plated layer 18	None	None	0.8
Example 28	Plated layer 18	None	Fe	0.8
Example 29	Plated layer 18	None	Ni	0.8
Example 30	Plated layer 1	None	Co	0.8
Example 31	Plated layer 2	None	Co	0.8
Example 32	Plated layer 3	None	Co	0.8
Example 33	Plated layer 4	None	Co	0.8
Example 34	Plated layer 5	None	Co	0.8
Example 35	Plated layer 6	None	Co	0.8
Example 36	Plated layer 7	None	Co	0.8
Example 37	Plated layer 8	None	Co	0.8
Example 38	Plated layer 9	None	Co	0.8
Example 39	Plated layer 10	None	Co	0.8
Example 40	Plated layer 11	None	Co	0.8
Example 41	Plated layer 12	None	Co	0.8
Example 42	Plated layer 13	None	Co	0.8

[0150]

[Table 3B]

	Zn-based plated layer			
	Type of plated layer	Pattern	Metal on surface of plated layer	Arithmetic average roughness Ra (μm)
Example 43	Plated layer 14	None	Co	0.8
Example 44	Plated layer 15	None	Co	0.8
Example 45	Plated layer 16	None	Co	0.8
Example 46	Plated layer 17	None	Co	0.8
Example 47	Plated layer 18	None	Co	0.8
Example 48	Plated layer 19	None	Co	0.8
Example 49	Plated layer 20	None	Co	0.8
Example 50	Plated layer 21	None	Co	0.8
Example 51	Plated layer 22	None	Co	0.8
Example 52	Plated layer 23	None	Co	0.8
Example 53	Plated layer 24	None	Co	0.8
Example 54	Plated layer 25	None	Co	0.8
Example 55	Plated layer 26	None	Co	0.8
Example 56	Plated layer 27	None	Co	0.8
Example 57	Plated layer 28	None	Co	0.8
Example 58	Plated layer 29	None	Co	0.8
Example 59	Plated layer 30	None	Co	0.8
Example 60	Plated layer 31	None	Co	0.8
Example 61	Plated layer 32	None	Co	0.8
Example 62	Plated layer 33	None	Co	0.8
Example 63	Plated layer 34	None	Co	0.8
Example 64	Plated layer 18	None	Co	0.8
Example 65	Plated layer 18	None	Co	0.8
Example 66	Plated layer 18	None	Co	0.8
Example 67	Plated layer 18	None	Co	0.8
Example 68	Plated layer 18	None	Co	0.8
Example 69	Plated layer 18	None	Co	0.8
Example 70	Plated layer 18	Pattern 1	Co	0.8
Example 71	Plated layer 18	Pattern 2	Co	0.8
Example 72	Plated layer 18	Pattern 3	Co	0.8
Example 73	Plated layer 18	Pattern 4	Co	0.8
Example 74	Plated layer 18	Pattern 4	Co	0.8
Comparative Example 1	Plated layer 18	None	Co	0.8
Comparative Example 2	Plated layer 18	None	Co	0.8
Comparative Example 3	Plated layer 18	None	Co	0.8
Comparative Example 4	Plated layer 18	None	Co	0.8
Comparative Example 5	Plated layer 18	None	Co	0.8
Comparative Example 6	Plated layer 18	None	Co	0.8
Comparative Example 7	Plated layer 18	None	Co	0.8
Comparative Example 8	Plated layer 18	None	Co	0.8
Comparative Example 9	Plated layer 18	None	Co	0.8
Comparative Example 10	Plated layer 18	None	Co	0.8
Comparative Example 11	Plated layer 18	None	Co	0.8

[0151]

[Table 4A]

	Chemical conversion treatment layer						
	Type of resin	20% or more	Average particle diameter (nm) of silica	Mass% of silica particles	Pigments	Pigments (mass%)	[Si]/[Cu] or [Si]/[Co] or [Si]/[Fe]
Example 1	Urethane resin	○	9	5	Cu-phthalocyanine	4.2	5
Example 2	Urethane resin	○	100	5	Cu-phthalocyanine	4.2	5
Example 3	Urethane resin	○	200	5	Cu-phthalocyanine	4.2	5
Example 4	Urethane resin	○	45	1	Cu-phthalocyanine	0.8	5
Example 5	Urethane resin	○	45	20	Cu-phthalocyanine	0.4	200
Example 6	Urethane resin	○	45	5	Co-phthalocyanine	4.5	5
Example 7	Urethane resin	○	45	5	Iron oxide	0.7	5
Example 8	Urethane resin	○	45	1	Cu-phthalocyanine	9.1	0.5
Example 9	Urethane resin	○	45	1	Cu-phthalocyanine	4.2	1
Example 10	Urethane resin	○	45	20	Cu-phthalocyanine	4.2	20
Example 11	Urethane resin	○	45	20	Cu-phthalocyanine	0.3	300
Example 12	Polyester resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 13	Epoxy resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 14	Phenol resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 15	Polyolefin resin (particle diameter of 0.1 μm)	○	45	5	Cu-phthalocyanine	4.2	5
Example 16	Fluorine resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 17	Acrylic resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 18	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 19	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 20	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 21	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 22	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 23	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 24	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 25	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 26	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 27	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 28	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 29	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 30	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5

Example 31	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 32	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 33	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 34	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 35	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 36	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 37	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 38	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 39	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 40	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 41	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 42	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 43	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5

[0152]

[Table 4B]

	Chemical conversion treatment layer						
	Type of resin	20% or more	Average particle diameter (nm) of silica	Mass% of silica particles	Pigments	Pigments (mass%)	[Si]/[Cu] or [Si]/[Co] or [Si]/[Fe]
Example 44	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 45	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 46	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 47	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 48	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 49	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 50	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 51	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 52	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 53	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 54	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 55	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 56	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 57	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 58	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 59	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 60	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 61	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 62	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 63	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 64	Urethane resin	○	45	5	Copper sulfate	1.2	5
Example 65	Urethane resin	○	45	5	Cobalt sulfate	1.1	5
Example 66	Urethane resin	○	45	5	Iron sulfate	1.3	5
Example 67	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 68	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 69	Urethane resin	○	5	5	Cu-phthalocyanine	4.2	5
Example 70	Urethane resin	○	45	5	Cu-phthalocyanine	4.2	5
Example 71	Urethane resin	○	45	1	Cu-phthalocyanine	0.8	5
Example 72	Urethane resin	○	45	1	Cu-phthalocyanine	0.8	5
Example 73	Urethane resin	○	45	1	Cu-phthalocyanine	0.8	5

Example 74	Urethane resin	○	45	1	Cu-phthalocyanine	11	250
Comparative Example 1	<u>None</u>	×	45	5	Cu-phthalocyanine	4.2	5
Comparative Example 2	Urethane resin	○	<u>None</u>	<u>0</u>	Cu-phthalocyanine	4.2	-
Comparative Example 3	Urethane resin	○	45	<u>30</u>	Cu-phthalocyanine	0.4	300
Comparative Example 4	Urethane resin	○	45	5	<u>None</u>	-	-
Comparative Example 5	Urethane resin	○	45	5	Copper sulfate	1.2	5
Comparative Example 6	Polyolefin resin (particle diameter of 0.8 μm)	○	45	5	Cu-phthalocyanine	4.2	5
Comparative Example 7	Urethane resin	○	<u>450</u>	5	Cu-phthalocyanine	4.2	5
Comparative Example 8	Urethane resin	○	45	5	<u>Carbon black</u>	4.2	-
Comparative Example 9	Urethane resin	○	45	5	<u>Quinacridone red</u>	4.2	-
Comparative Example 10	Urethane resin	○	45	5	<u>Bismuth vanadium</u>	4.2	-
Comparative Example 11	Urethane resin	○	45	5	<u>Titanium oxide</u>	4.2	-

The lower line portion indicates that the data is out of the range of the present invention.

[0153]

[Table 5A]

	Chemical conversion treatment layer							
	Nb-oxide	Na-phosphate	Arithmetic average height Sa (nm)	Deposition amount of chemical conversion treatment layer (g/m ²)	b*	L*	Metal luster feeling	60-degree mirror surface glossiness G _s (60°)
Example 1	○	○	10	1.5	AAA	AAA	AA	A
Example 2	○	○	10	1.5	AAA	AA	AA	A
Example 3	○	○	10	1.5	AAA	A	A	A
Example 4	○	○	10	1.5	AA	AAA	AA	A
Example 5	○	○	10	1.5	AA	AA	A	A
Example 6	○	○	10	1.5	AAA	AAA	AA	A
Example 7	○	○	10	1.5	AA	AAA	AA	A
Example 8	○	○	10	1.5	AA	AAA	AA	A
Example 9	○	○	10	1.5	AAA	AAA	AA	A
Example 10	○	○	10	1.5	AAA	AA	AA	A
Example 11	○	○	10	1.5	AAA	AA	AA	A
Example 12	○	○	10	1.5	AAA	AAA	AA	A
Example 13	○	○	10	1.5	AAA	AAA	AA	A
Example 14	○	○	10	1.5	AAA	AAA	AA	A
Example 15	○	○	10	1.5	AAA	AAA	AA	A
Example 16	○	○	10	1.5	AAA	AAA	AA	A
Example 17	○	○	10	1.5	AAA	AAA	AA	A
Example 18	None	○	10	1.5	AAA	AAA	AA	A
Example 19	○	None	10	1.5	AAA	AAA	AA	A
Example 20	None	None	10	1.5	AAA	AAA	AA	A
Example 21	○	○	5	1.5	AAA	AAA	AA	A
Example 22	○	○	20	1.5	AAA	AAA	AA	A
Example 23	○	○	25	1.5	AAA	AAA	A	A
Example 24	○	○	10	1.5	AAA	AAA	AA	A
Example 25	○	○	10	1.5	AAA	AAA	AA	A
Example 26	○	○	10	1.5	AAA	AA	AA	A
Example 27	○	○	10	1.5	AA	AAA	AA	A
Example 28	○	○	10	1.5	AAA	AAA	AA	A
Example 29	○	○	10	1.5	AAA	AAA	AA	A
Example 30	○	○	10	1.5	AAA	AAA	AA	A
Example 31	○	○	10	1.5	AAA	AAA	AA	A
Example 32	○	○	10	1.5	AAA	AAA	AA	A
Example 33	○	○	10	1.5	AAA	AAA	AA	A
Example 34	○	○	10	1.5	AAA	AAA	AA	A
Example 35	○	○	10	1.5	AAA	AAA	AA	A
Example 36	○	○	10	1.5	AAA	AAA	AA	A
Example 37	○	○	10	1.5	AAA	AAA	AA	A
Example 38	○	○	10	1.5	AAA	AAA	AA	A
Example 39	○	○	10	1.5	AAA	AAA	AA	A
Example 40	○	○	10	1.5	AAA	AAA	AA	A
Example 41	○	○	10	1.5	AAA	AAA	AA	A
Example 42	○	○	10	1.5	AAA	AAA	AA	A
Example 43	○	○	10	1.5	AAA	AAA	AA	A

[0154]

[Table 5B]

	Chemical conversion treatment layer							
	Nb-oxide	Na-phosphate	Arithmetic average height Sa (nm)	Deposition amount of chemical conversion treatment layer (g/m ²)	b*	L*	Metal luster feeling	60-degree mirror surface glossiness G _s (60°)
Example 44	○	○	10	1.5	AAA	AAA	AA	A
Example 45	○	○	10	1.5	AAA	AAA	AA	A
Example 46	○	○	10	1.5	AAA	AAA	AA	A
Example 47	○	○	10	1.5	AAA	AAA	AA	A
Example 48	○	○	10	1.5	AAA	AAA	AA	A
Example 49	○	○	10	1.5	AAA	AAA	AA	A
Example 50	○	○	10	1.5	AAA	AAA	AA	A
Example 51	○	○	10	1.5	AAA	AAA	AA	A
Example 52	○	○	10	1.5	AAA	AAA	AA	A
Example 53	○	○	10	1.5	AAA	AAA	AA	A
Example 54	○	○	10	1.5	AAA	AAA	AA	A
Example 55	○	○	10	1.5	AAA	AAA	AA	A
Example 56	○	○	10	1.5	AAA	AAA	AA	A
Example 57	○	○	10	1.5	AAA	AAA	AA	A
Example 58	○	○	10	1.5	AAA	AAA	AA	A
Example 59	○	○	10	1.5	AAA	AAA	AA	A
Example 60	○	○	10	1.5	AAA	AAA	AA	A
Example 61	○	○	10	1.5	AAA	AAA	AA	A
Example 62	○	○	10	1.5	AAA	AAA	AA	A
Example 63	○	○	10	1.5	AAA	AAA	AA	A
Example 64	○	○	10	1.5	AA	AAA	AA	A
Example 65	○	○	10	1.5	AA	AAA	AA	A
Example 66	○	○	10	1.5	AA	AAA	AA	A
Example 67	○	○	5	0.1	AAA	AAA	AA	A
Example 68	○	○	5	15	AAA	AA	A	A
Example 69	○	○	10	1.5	AAA	AAA	AA	A
Example 70	○	○	10	1.5	AAA	AAA	AA	A
Example 71	○	○	10	1.5	AAA	AAA	AA	A
Example 72	○	○	10	1.5	AAA	AAA	AA	A
Example 73	○	○	10	1.5	AAA	AAA	AA	A
Example 74	○	○	10	1.5	A	A	A	A
Comparative Example 1	○	○	10	1.5	AAA	AA	AA	A
Comparative Example 2	○	○	10	1.5	AAA	AA	AA	A
Comparative Example 3	○	○	10	1.5	AA	B	B	A
Comparative Example 4	○	○	10	1.5	<u>B</u>	AA	A	A
Comparative Example 5	○	○	10	1.5	<u>B</u>	AAA	AA	A
Comparative Example 6	○	○	50	1.5	AAA	A	B	<u>B</u>
Comparative Example 7	○	○	10	1.5	AAA	AAA	B	A
Comparative Example 8	○	○	10	1.5	<u>B</u>	B	A	A
Comparative Example 9	○	○	10	1.5	<u>B</u>	A	A	A
Comparative Example 10	○	○	10	1.5	<u>B</u>	A	A	A
Comparative Example 11	○	○	10	1.5	<u>B</u>	A	A	A

The lower line portion indicates that the data is out of the range of the present invention.

[0155]

[Table 6A]

	Backening resistance	Corrosion resistance	Metallic appearance	Weather resistance
Example 1	4	4	4	3
Example 2	4	4	4	3
Example 3	4	4	4	3
Example 4	4	4	4	3
Example 5	4	4	4	3
Example 6	4	4	4	3
Example 7	4	4	4	3
Example 8	4	3	4	3
Example 9	4	4	4	3
Example 10	4	4	4	3
Example 11	4	4	3	3
Example 12	4	4	4	3
Example 13	4	4	4	3
Example 14	4	4	4	4
Example 15	4	4	4	4
Example 16	4	4	4	4
Example 17	4	4	4	4
Example 18	4	3	4	3
Example 19	4	3	4	3
Example 20	4	3	4	3
Example 21	4	4	4	3
Example 22	4	4	4	3
Example 23	4	4	3	3
Example 24	4	4	4	3
Example 25	4	4	4	3
Example 26	4	4	3	3
Example 27	3	4	4	3
Example 28	4	4	4	3
Example 29	4	4	4	3
Example 30	4	3	4	3
Example 31	4	3	4	3
Example 32	4	3	4	3
Example 33	4	3	4	3
Example 34	4	3	4	3
Example 35	4	3	4	3
Example 36	4	3	4	3
Example 37	4	4	4	3
Example 38	4	4	4	3
Example 39	4	4	4	3
Example 40	4	4	4	3
Example 41	4	3	4	3
Example 42	4	4	4	3
Example 43	4	4	4	3

[0156]

[Table 6B]

	Backening resistance	Corrosion resistance	Metallic appearance	Weather resistance
Example 44	4	4	4	3
Example 45	4	3	4	3
Example 46	4	4	4	3
Example 47	4	4	4	3
Example 48	4	4	4	3
Example 49	4	4	4	3
Example 50	4	4	4	3
Example 51	4	4	4	3
Example 52	4	4	4	3
Example 53	4	4	4	3
Example 54	4	3	4	3
Example 55	4	3	4	3
Example 56	4	4	4	3
Example 57	4	4	4	3
Example 58	4	4	4	3
Example 59	4	4	4	3
Example 60	4	4	4	3
Example 61	4	4	4	3
Example 62	4	4	4	3
Example 63	4	4	4	3
Example 64	3	4	4	3
Example 65	3	4	4	3
Example 66	3	4	4	3
Example 67	4	4	4	3
Example 68	4	4	4	3
Example 69	4	4	4	3
Example 70	4	4	4	3
Example 71	4	4	4	3
Example 72	4	4	4	3
Example 73	4	4	4	3
Example 74	3	4	3	3
Comparative Example 1	It was impossible to perform evaluation due to brittleness of chemical conversion film.			
Comparative Example 2	4	1	4	3
Comparative Example 3	It was impossible to perform evaluation due to brittleness of chemical conversion film.			
Comparative Example 4	1	4	4	3
Comparative Example 5	3	4	1	3
Comparative Example 6	3	4	1	4
Comparative Example 7	4	4	1	3
Comparative Example 8	1	3	3	3
Comparative Example 9	1	4	3	3
Comparative Example 10	1	3	3	3
Comparative Example 11	1	4	3	3

[0157]

As shown in Tables 1 to 6B, the Zn-based plated steel sheets of Examples 1 to 74 all had a chemical conversion treatment layer that satisfies the scope of the present

invention, and had favorable blackening resistance, corrosion resistance, metallic appearance, and weather resistance.

In addition, the Zn-based plated steel sheets of Examples 14 to 16 using a phenolic resin, a polyolefin resin, a fluorine resin, or an acrylic resin as a resin contained
5 in the chemical conversion treatment layers had particularly excellent weather resistance.

Furthermore, in Examples 70 to 74 in which a pattern portion was formed on a plated layer, the blackening resistance, the corrosion resistance, the metallic appearance, and the weather resistance were favorable and the visibility of the pattern portion was greatly improved.

10 [0158]

On the other hand, as shown in Tables 1 to 6B, in Comparative Example 1, since the chemical conversion treatment layer did not contain a resin, the chemical conversion treatment layer itself became very brittle, and various evaluation tests could not be carried out.

15 Since Comparative Example 2 did not contain silica particles, the corrosion resistance deteriorated.

In Comparative Example 3, since the amount of silica particles was as high as 30%, the chemical conversion treatment layer itself became very brittle, and various evaluation tests could not be carried out.

20 In Comparative Example 4, since no pigment was contained in the chemical conversion treatment layer, the blackening resistance deteriorated.

In Comparative Example 5, the b^* of the chemical conversion treatment layer was out of a range of -30 to -2 because the drying conditions during the formation of the chemical conversion treatment layer were out of the preferable range, resulting in
25 insufficient metallic appearance.

In Comparative Example 6, the 60-degree mirror surface glossiness G_s (60°) of the surface of the chemical conversion treatment layer was out of a range of 50 to 200 because the drying conditions during the formation of the chemical conversion treatment layer were out of the preferable range, resulting in insufficient metallic appearance.

5 In Comparative Example 7, since the diameter of silica particles was 450 nm, the metallic appearance was insufficient.

Comparative Examples 8 to 11 did not contain a pigment containing Cu, Co, or Fe, and the blackening resistance was insufficient.

[Industrial Applicability]

10 [0159]

 According to the present invention, it is possible to provide a Zn-based plated steel sheet which contains Al and in which, even if a plated surface partially or wholly turns black due to oxidation of Al contained in the plated layer, the blackening can be made less noticeable to maintain the metallic appearance, and corrosion resistance and
15 weather resistance are improved. Therefore, the present invention has high industrial applicability.

[CLAIMS]

1. A Zn-based plated steel sheet comprising:

a steel sheet;

5 a Zn-based plated layer which contains Zn and 0.05 to 60 mass% of Al and is placed on at least one surface of the steel sheet; and

a chromate-free chemical conversion treatment layer which has a deposition amount of 0.1 to 15 g/m² per surface and is placed on the Zn-based plated layer,

10 wherein the chemical conversion treatment layer contains 20 mass% or more of a resin, 1 to 20 mass% of silica particles having an average particle diameter of 5 to 200 nm, and a pigment containing one or more of Cu, Co, or Fe, and

15 wherein b* of an appearance of the Zn-based plated steel sheet evaluated in a CIE 1976 (L*, a*, b*) color space is -30 to -2, a 60-degree mirror surface glossiness G_s (60°) specified in JIS Z 8741:1997 is 50 to 200, and the Zn-based plated steel sheet exhibits a metallic appearance.

2. The Zn-based plated steel sheet according to claim 1,

wherein the pigment is any one or more of copper(II) phthalocyanine, cobalt(II) phthalocyanine, copper sulfate, cobalt sulfate, iron sulfate, and iron oxide.

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3. The Zn-based plated steel sheet according to claim 1 or 2,

wherein [Si]/([Cu]+[Co]+[Fe]) is within a range of 1 to 200 as a mixing ratio between the silica particles and the pigment in the chemical conversion treatment layer in a case where an equivalent amount of Si in the silica particles is represented by [Si] and

equivalent amounts of Cu, Co, and Fe in the pigment are respectively represented by [Cu], [Co], and [Fe].

4. The Zn-based plated steel sheet according to any one of claims 1 to 3,

5 wherein an arithmetic average roughness Ra of the Zn-based plated layer is 0.5 to 2.0 μm and an arithmetic average height Sa of the chemical conversion treatment layer is 5 nm to 100 nm.

5. The Zn-based plated steel sheet according to any one of claims 1 to 4,

10 wherein the chemical conversion treatment layer further contains either one or both of an Nb compound and a phosphoric acid compound.

6. The Zn-based plated steel sheet according to any one of claims 1 to 5,

15 wherein the resin in the chemical conversion treatment layer includes any one or more of a polyolefin resin, a fluororesin, an acrylic resin, a urethane resin, a polyester resin, an epoxy resin, and a phenol resin.

7. The Zn-based plated steel sheet according to any one of claims 1 to 6,

20 wherein the Zn-based plated layer contains 4 mass% to 22 mass% of Al, 1 mass% to 10 mass% of Mg, and the balance being Zn and impurities in an average composition.

8. The Zn-based plated steel sheet according to any one of claims 1 to 7,

25 wherein the Zn-based plated layer further contains 0.0001 to 2 mass% of Si in an average composition.

9. The Zn-based plated steel sheet according to any one of claims 1 to 8,
wherein the Zn-based plated layer further contains one or more of Ni, Sb, and Pb
in a total of 0.0001 to 2 mass% in an average composition.

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10. The Zn-based plated steel sheet according to any one of claims 1 to 9,
wherein a non-pattern portion and a pattern portion placed to have a
predetermined shape are formed on the Zn-based plated layer,

wherein the pattern portion and the non-pattern portion each contain one or two
10 of a first region and a second region determined by any of determination methods 1 to 5
below, and

wherein an absolute value of a difference between an area proportion of the first
region in the pattern portion and an area proportion of the first region in the non-pattern
portion is 30% or more,

15 (Determination method 1)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals
of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region
partitioned by the virtual grid lines is defined as a measurement region A, an L^* -value in
each measurement region A is measured, and when arbitrary 50 points are selected from
20 the obtained L^* -values and an average of the obtained L^* -values at the 50 points is
defined as a standard L^* -value, a region in which the L^* -value is equal to or more than
the standard L^* -value is defined as a first region and a region in which the L^* -value is less
than the standard L^* -value is defined as a second region,

(Determination method 2)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, a circle with a diameter of 0.5 mm centered at a centroid point of each region partitioned by the virtual grid lines is defined as a measurement region A, an L^* -value in each measurement region A is measured, a region in which the L^* -value is 45 or more is defined as a first region, and a region in which the L^* -value is less than 45 is defined as a second region,

(Determination method 3)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 0.5 mm, an arithmetic average height Sa_2 is measured in each of a plurality of regions partitioned by the virtual grid lines, a region in which the obtained arithmetic average height Sa_2 is 1 μm or more is defined as a first region, and a region in which the obtained arithmetic average height Sa_2 is less than 1 μm is defined as a second region,

(Determination method 4)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a plane (0002) of a Zn phase and a diffraction peak intensity I_{10-11} of a plane (10-11) of the Zn phase are measured for each region through an X-ray diffraction method in which X-rays are respectively made to be incident on the plurality of regions partitioned by the virtual grid lines, a proportion of these intensities (I_{0002}/I_{10-11}) is defined as an orientation rate, a region in which the orientation rate is 3.5 or more is defined as a first region, and a region in which the orientation rate is less than 3.5 is defined as a second region, and

(Determination method 5)

Virtual grid lines are drawn on a surface of the Zn-based plated layer at intervals of 1 mm, a circle S centered at a centroid point G of each region is drawn for each of a plurality of regions partitioned by the virtual grid lines, a diameter R of the circle S is set

so that a total length of surface boundary lines of the Zn-based plated layer contained in the circle S is 10 mm, an average value of a maximum diameter $R_{\max}$ and a minimum diameter $R_{\min}$ among diameters R of circles S in the plurality of regions is defined as a standard diameter R_{ave} , a region having a circle S of which the diameter R is less than 5 the standard diameter R_{ave} is defined as a first region, and a region having a circle S of which the diameter R is greater than or equal to the standard diameter R_{ave} is defined as a second region.

11. The Zn-based plated steel sheet according to any one of claims 1 to 10,
10 wherein the Zn-based plated layer has any one or more of Co, Fe, and Ni on its surface.