

[Specification]

[Title of Invention]

Zn-BASED PLATED STEEL SHEET

[Technical Field]

[0001]

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

[Background Art]

[0002]

Among plated steel sheets that are mostly used as plated steel sheets having satisfactory corrosion resistance, there are Zn-based plated steel sheets. These Zn-based plated steel sheets are used in various manufacturing industries such as automobiles, home appliances, and building material fields. Among them, particularly, an amount of Al-added plating used 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 describes a hot-dip Zn-Al-Mg-Si plated steel sheet. This plated steel sheet has an appearance of a pear-skin pattern and is characterized by being excellent in aesthetic appearance.

[0004]

Incidentally, conventionally, a chromate treatment using hexavalent chromate or the like has been widely performed after plating to give a further advanced rust preventive function to a Zn-based plated steel sheet,

and furthermore, coating with an organic resin has been performed to give a high value-added function such as a design, contamination resistance, and lubricity as appropriate. However, due to the background of increase in environmental problems, there is a movement to refrain from using the chromate treatment. Therefore, for the purpose of easily giving an advanced rust preventive function only with a single layer treatment of a resin-based film without performing the chromate treatment, a surface-treated plated steel sheet is described in Patent Document 2 below. When the film described in Patent Document 2 below is used, it is possible to further improve corrosion resistance.

[0005]

Incidentally, in recent years, there has been a demand for further improvement in aesthetic appearance of the Zn-based plated steel sheet containing Al. Specifically, a surface of the Zn-based plated steel sheet exhibits an achromatic color-based pear-skin pattern in which glossy portions and white portions are mixed, but there is a demand for a golden appearance to give gorgeousness in appearance.

[Citation List]

[Patent Document]

[0006]

[Patent Document 1]

Japanese Patent No. 3179446

[Patent Document 2]

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

[Summary of the Invention]

[Problems to be Solved by the Invention]

[0007]

The present invention has been made in view of the above circumstances, and an objective of the present invention is to provide a Zn-based plated steel sheet exhibiting a golden appearance with a sense of luxury and having improved corrosion resistance in Zn-based plated steel sheets containing Al.

[Means for Solving the Problem]

[0008]

In order to solve the above-described problem, the present inventors have conducted intensive studies and found that by reducing a surface roughness of the Zn-based plated layer to give it metallic luster and then making a yellow colorant be contained in a chemical conversion treatment layer, it appears gold to the naked eye. The present invention employs the following configurations.

[0009]

[1] A Zn-based plated steel sheet including

a steel sheet,

a Zn-based plated layer disposed on at least one side of the steel sheet and containing 0.05 to 60% by mass of Al, and Zn, and

at least one layer of a chromate-free chemical conversion treatment layer disposed on the Zn-based plated layer with an adhesion amount per side of 0.1 to 15 g/m², in which

the chemical conversion treatment layer contains a resin and a

yellow colorant,

when an appearance is evaluated in a CIE 1976 (L^* , a^* , b^*) color space, b^* is 2 or higher and 60 or lower and b^*/a^* is -3 or higher and 3 or lower, and a 60-degree mirror surface glossiness G_s (60°) defined by JIS Z 8741:1997 is 50 to 200, and

in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 , L^*1 and L^*2 satisfy the following Expression 1.

$$10 \geq L^*1/L^*2 \geq 2 \cdots \text{Expression 1}$$

[2] The Zn-based plated steel sheet according to above-described [1], in which the yellow colorant may be an azo-based yellow pigment or an iron oxide-based yellow pigment.

[3] The Zn-based plated steel sheet according to above-described [1] or [2], in which an amount of the yellow colorant in the chemical conversion treatment layer may be 0.1 to 10% by mass.

[4] The Zn-based plated steel sheet according to any one of above-described [1] to [3], in which L^*1 and L^*2 may satisfy the following Expression 2.

$$7 \geq L^*1/L^*2 \geq 4 \cdots \text{Expression 2}$$

[5] The Zn-based plated steel sheet according to any one of above-described [1] to [4], in which the chemical conversion treatment layer may contain 1

to 20% by mass of metal oxide particles having an average particle size of 5 to 200 nm and a refractive index of 1.3 to 2.5.

[6] The Zn-based plated steel sheet according to above-described [5], in which the metal oxide particles may include silica particles.

[7] The Zn-based plated steel sheet according to above-described [5] or [6], in which a mixing ratio of the yellow colorant and the metal oxide particles in the chemical conversion treatment layer may be in a range of 1 to 200.

[8] The Zn-based plated steel sheet according to any one of above-described [1] to [7], in which an arithmetic average roughness Ra on a surface of the Zn-based plated layer may be 0.1 to 2.0 μm .

[9] The Zn-based plated steel sheet according to any one of above-described [1] to [8], in which the arithmetic average roughness Ra of the Zn-based plated layer may be 0.5 to 2.0 μm , and an arithmetic average height Sa of the chemical conversion treatment layer may be 5 nm to 100 nm.

[10] The Zn-based plated steel sheet according to any one of above-described [1] to [9], in which the chemical conversion treatment layer may further contain either one or both of a Nb compound and a phosphate compound.

[11] The Zn-based plated steel sheet according to any one of above-described [1] to [10], in which the resin in the chemical conversion treatment layer may include one or more of a polyolefin resin, a fluorine resin, an acrylic resin, a urethane resin, a polyester resin, an epoxy resin, and a phenol resin.

[12] The Zn-based plated steel sheet according to any one of above-described [1] to [11], in which the Zn-based plated layer may contain, in an

average composition, 4% by mass or more and 22% by mass or less of Al, more than 1% by mass and 10% by mass or less of Mg, and a balance being Zn and impurities.

[13] The Zn-based plated steel sheet according to any one of above-described [1] to [12], in which the Zn-based plated layer may further contain, in an average composition, 0.0001 to 2% by mass of Si.

[14] The Zn-based plated steel sheet according to any one of above-described [1] to [13], in which the Zn-based plated layer may further contain, in an average composition, one or more of Ni, Sb, and Pb in an amount of 0.0001 to 2% by mass in total.

[15] The Zn-based plated steel sheet according to any one of above-described [1] to [14], in which when L^* in a range of 0.5 mm in diameter centered at each point is measured for arbitrary five points on the plated surface, a maximum value of L^* may be 1.2 times or more a minimum value of L^* .

[16] The Zn-based plated steel sheet according to any one of above-described [1] to [15], in which

a patterned portion disposed to have a predetermined shape and a non-patterned portion may be formed on the Zn-based plated layer,

the patterned portion and the non-patterned portion may each include one or two of a first region and a second region determined by any of the following determination methods 1 to 5, and

an absolute value of a difference between an area ratio of the first region in the patterned portion and an area ratio of the first region in the non-patterned portion may be 30% or more.

[Determination method 1]

Virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, an inside of a circle with a diameter of 0.5 mm centered at a centroid point of each region of a plurality of regions partitioned by the virtual lattice lines is defined as a measurement region A, and an L^* value in each measurement region A is measured. When 50 points are selected arbitrarily from the obtained L^* values and an average of the 50 points of the obtained L^* values is used as a reference L^* value, a region in which the L^* value is equal to or higher than the reference L^* value is defined as the first region, and a region in which the L^* value is lower than the reference L^* value is defined as the second region.

[Determination method 2]

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

[Determination method 3]

Virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, and an arithmetic average surface roughness S_a is measured in each of a plurality of regions partitioned by the virtual lattice lines. A region in which the obtained S_a is 1 μm or more is defined as the

first region, and a region in which the obtained Sa is less than 1 μm is defined as the second region.

[Determination method 4]

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

[Determination method 5]

Virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 1 mm, and then 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 lattice 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 included inside the circle S is 10 mm. An average value of a maximum diameter R_{max} and a minimum diameter R_{min} of the diameters R of the circles S in the plurality of regions is defined as a reference diameter R_{ave} , a region having the circle S with the diameter R smaller than the reference diameter R_{ave} is defined as the first region, and a region having the circle S with the diameter R equal to or larger than the reference diameter R_{ave} is defined as

the second region.

[17] The Zn-based plated steel sheet according to any one of above-described [1] to [16], in which the surface of the Zn-based plated layer may contain any one of Co, Fe, and Ni.

[Effects of the Invention]

[0010]

According to the present invention, in Zn-based plated steel sheets containing Al, a Zn-based plated steel sheet exhibiting a golden appearance with a sense of luxury and having improved corrosion resistance can be provided.

[Embodiment for implementing the Invention]

[0011]

The present inventors have found that, when a chemical conversion treatment layer is made to contain a yellow colorant to color the chemical conversion treatment layer yellow, and a surface roughness of a Zn-based plated layer is reduced to exhibit metallic luster, an appearance of the Zn-based plated layer becomes gold to the naked eye. However, it has been found that if the yellow color is too dark, a metallic appearance on a surface of the plated layer becomes difficult to be recognized and the whole appears yellow, and an appearance of the color of the Zn-based plated layer changes depending on whether incident light is reflected on the surface of the plated layer or incident light is reflected on a surface of the chemical conversion treatment layer and does not look gold. As a result of further studies, it has been found that a golden appearance is obtained when a b^* value and b^*/a^* in a case of being evaluated in the CIE 1976 (L^* , a^* , b^*) color space

and a 60-degree mirror surface glossiness G_s (60°) defined by JIS Z 8741:1997 are controlled to be within a predetermined range, and when L^*1 and L^*2 are controlled to satisfy $10 \geq L^*1/L^*2 \geq 2$ (Expression 1) provided that, in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 . Also, it has also been found that, even when an arbitrary shape such as letters is displayed on the surface of the plated layer, the arbitrary shape can be made easier to see by controlling a relationship between the b^* value and b^*/a^* , the 60-degree mirror surface glossiness G_s (60°), and L^*1 and L^*2 . As a result, fine particles of gold or metal fine particles exhibiting gold do not need to be contained in the chemical conversion treatment layer, and a golden appearance can be obtained at low cost.

[0012]

That is, a Zn-based plated steel sheet according to an embodiment of the present invention is a Zn-based plated steel sheet that includes a steel sheet, a Zn-based plated layer disposed on at least one side of the steel sheet and containing 0.05 to 60% by mass of Al, and Zn, and at least one layer of a chromate-free chemical conversion treatment layer disposed on the Zn-based plated layer with an adhesion amount per side of 0.1 to 15 g/m², in which the chemical conversion treatment layer contains a resin and a yellow

colorant, when an appearance is evaluated in the CIE 1976 (L^* , a^* , b^*) color space, b^* is 2 or higher and 60 or lower and b^*/a^* is -10 or higher and -3 or lower, and a 60-degree mirror surface glossiness G_s (60°) defined by JIS Z 8741:1997 is 50 to 200, and, in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 , in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters on the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 , L^*1 and L^*2 satisfy $10 \geq L^*1/L^*2 \geq 2$ (Expression 1).

Also, in the Zn-based plated steel sheet of the present embodiment, the yellow colorant is preferably an azo-based yellow pigment or an iron oxide-based yellow pigment.

Also, in the Zn-based plated steel sheet of the present embodiment, an amount of the yellow colorant in the chemical conversion treatment layer is preferably 0.1 to 10% by mass.

Also, in the Zn-based plated steel sheet of the present embodiment,

L^*1 and L^*2 preferably satisfy $7 \geq L^*1/L^*2 \geq 4$ (Expression 2).

Also, in the Zn-based plated steel sheet of the present embodiment, the chemical conversion treatment layer preferably contains 1 to 20% by mass of metal oxide particles having an average particle size of 5 to 200 nm and a refractive index of 1.3 to 2.5.

Also, in the Zn-based plated steel sheet of the present embodiment, the metal oxide particles preferably include silica particles.

Also, in the Zn-based plated steel sheet of the present embodiment, a mixing ratio of the yellow colorant and the metal oxide particles is preferably in a range of 1 to 200.

Also, in the Zn-based plated steel sheet of the present embodiment, an arithmetic average roughness Ra on a surface of the Zn-based plated layer is preferably 0.1 to 2.0 μm .

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

[0013]

[Zn-based plated steel sheet]

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

A material of a steel sheet serving as a base of a Zn-based plated layer is not particularly limited. As the material, general steel can be used without any particular limitation, Al-killed steel or some high-alloy steels can also be applied, and a shape is also not particularly limited. The Zn-

based plated layer according to the present embodiment is formed by applying a hot-dip plating method, which will be described later, to a steel sheet.

[0014]

[Zn-based plated layer]

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

The Zn-based plated layer is a Zn-based plated layer containing 0.05 to 60% by mass of Al, and Zn. Also, the Zn-based plated layer of the present embodiment preferably contains, in an average composition, 4 to 22% by mass of Al and 1 to 10% by mass of Mg, and contains Zn and impurities as a balance. It is more preferable that, in an average composition, 4 to 22% by mass of Al, more than 1% by mass and 10% by mass or less of Mg, and the balance being Zn and impurities be contained.

[0015]

When Al is contained in an amount of 0.05% by mass or more, corrosion resistance of the Zn-based plated layer can be improved, and when the Al content is set to 60% by mass or less, it is possible to relatively increase an amount of Zn contained in the Zn-based plated layer, thereby securing sacrificial corrosion resistance. Also, when 4 to 22% by mass of Al, 1 to 10% by mass of Mg, and a balance of Zn and impurities are contained, corrosion resistance and sacrificial corrosion resistance can be further improved. The Zn-based plated layer may contain 40% by mass or more of Zn.

[0016]

Also, the Zn-based plated layer may contain 0.001 to 2% by mass of Si in an average composition. Further, the Zn-based plated layer may contain, in an average composition, one or more of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C in an amount of 0.001 to 2% by mass in total.

[0017]

Next, the reason for limiting a composition of the Zn-based plated layer to a Zn-based plated layer containing 4 to 22% by mass of Al, more than 1% by mass and 10% by mass or less of Mg, and a balance being Zn and impurities will be described.

[0018]

The Al content is in a range of 4 to 22% by mass. Al is preferably contained to secure corrosion resistance. If the Al content in the Zn-based plated layer is 4% by mass or more, an effect of improving corrosion resistance is further enhanced. When the Al content is 22% by mass or less, an effect of improving corrosion resistance is likely to be secured while maintaining a golden appearance. From the perspective of corrosion resistance, 5 to 18% by mass is preferable. 6 to 16% by mass is more preferable.

[0019]

The Mg content is in a range of more than 1% by mass and 10% by mass or less. Mg is preferably contained to improve corrosion resistance. If the Mg content in the Zn-based plated layer is more than 1% by mass, an effect of improving corrosion resistance is further enhanced. When the Mg content is 10% by mass or less, generation of dross in a plating bath is

suppressed, thereby making it easier to stably produce a Zn-based plated steel sheet. From the perspective of a balance between corrosion resistance and generation of dross, the Mg content is preferably 1.5 to 6% by mass. More preferably, the Mg content is in a range of 2 to 5% by mass.

[0020]

A Zn-based plated layer containing Mg tends to turn black, but on the other hand, since the turning black brings out a depth of color if a chemical conversion treatment layer containing a yellow colorant is disposed on the plated layer, there is an advantage in that a gold color having better sense of luxury is obtained.

[0021]

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

[0022]

Also, the Zn-based plated layer may contain Si in a range of 0.0001 to 2% by mass.

Since Si may enhance adhesion of the Zn-based plated layer, Si may be contained. Since the effect of enhancing adhesion is exhibited when Si is contained in an amount of 0.0001% by mass or more, preferably 0.001% or more, more preferably 0.01% or more, it is preferable that 0.0001% by mass or more of Si be contained. On the other hand, since the effect of enhancing plating adhesion is saturated even when the Si content exceeds

2% by mass, the Si content is set to be 2% by mass or less. From the perspective of plating adhesion, the Si content may be in a range of 0.001 to 1% by mass and may be in a range of 0.01 to 0.8% by mass.

[0023]

The Zn-based plated layer may contain, in an average composition, one or more of Ni, Ti, Zr, Sr, Fe, Sb, Pb, Sn, Ca, Co, Mn, P, B, Bi, Cr, Sc, Y, REM, Hf, and C in an amount of 0.001 to 2% by mass in total. When these elements are contained, corrosion resistance can be further improved.

REM is one or more of the rare-earth elements with atomic numbers 57 to 71 in the periodic table.

[0024]

The balance of the chemical composition of the Zn-based plated layer is zinc and impurities. Impurities include those that are inevitably contained in zinc or other base metals, and those that are contained by dissolution of steel in the plating bath.

[0025]

Further, an average composition of the Zn-based plated layer can be measured by the following method. First, after a surface layer coating film is removed with a coating film remover (for example, a Neo rever SP-751 manufactured by Sansai Kako Co., Ltd.) that does not corrode plating, the Zn-based plated layer is dissolved with hydrochloric acid containing an inhibitor (Hibiron manufactured by Sugimura Chemical Industrial Co., Ltd.), and the average composition can be obtained by subjecting the obtained solution to an inductively coupled plasma (ICP) emission spectroscopy method. When the surface layer coating film is removed, it is

preferable to also remove a chemical conversion treatment layer.

[0026]

Next, a structure of the Zn-based plated layer will be described.

The structure described below is a structure when the Zn-based plated layer contains, in an average composition, 4 to 22% by mass of Al, 1 to 10% by mass of Mg, and 0 to 2% by mass of Si.

[0027]

The Zn-based plated layer containing Al, Mg, and Zn contains an [Al phase] and an [Al/Zn/MgZn₂ ternary eutectic structure]. This has a form in which the [Al phase] is included in the base of the [Al/Zn/MgZn₂ ternary eutectic structure]. Further, a [MgZn₂ phase] or a [Zn phase] may be included in the base of the [Al/Zn/MgZn₂ ternary eutectic structure]. Also, when Si is added, a [Mg₂Si phase] may be included in the base of the [Al/Zn/MgZn₂ ternary eutectic structure].

[0028]

Here, the [Al/Zn/MgZn₂ ternary eutectic structure] refers to a ternary eutectic structure of an Al phase, a Zn phase, and an intermetallic compound MgZn₂ phase, and the Al phase forming the ternary eutectic structure corresponds to, for example, an “Al” phase (Al solid solution in which Zn is dissolved and a small amount of Mg is contained) at a high temperature in a ternary equilibrium diagram of Al-Zn-Mg. The “Al” phase at the high temperature usually appears to be separated into a fine Al phase and a fine Zn phase at room temperature. Also, the Zn phase in the ternary eutectic structure is a Zn solid solution in which a small amount of Al is dissolved and, in some cases, even smaller amount of Mg is also dissolved.

The MgZn_2 phase in the ternary eutectic structure is an intermetallic compound phase that is present in the vicinity of about 84% by mass of Zn in a binary equilibrium diagram of Zn-Mg. As far as viewed from the phase diagram, it is thought that other additive elements are not dissolved in each of the phases or the amount is extremely small even if they are dissolved, but since the amount cannot be clearly distinguished by an ordinary analysis, the ternary eutectic structure consisting of these three phases is referred to as [Al/Zn/MgZn₂ ternary eutectic structure] in the present specification.

[0029]

Also, the [Al Phase] refers to a phase that is visible in an island shape with a clear boundary in the base of the above-described ternary eutectic structure, and this corresponds to, for example, an “Al” phase” (Al solid solution in which Zn is dissolved and a small amount of Mg is contained) at a high temperature in the ternary equilibrium diagram of Al-Zn-Mg. The Al” phase at the high temperature is different in amount of Zn or Mg dissolved therein according to Al and Mg concentrations of the plating bath. The Al” phase at the high temperature is usually separated into a fine Al phase and a fine Zn phase at room temperature, but the island-like shape that is visible at room temperature can be considered to be a shape retaining the shape of the Al” phase at the high temperature. As far as viewed from the phase diagram, it is thought that other additive elements are not dissolved in the phase or the amount is extremely small even if they are dissolved, but since they cannot be clearly distinguished by an ordinary analysis, the phase derived from the Al” phase at the high temperature and

retaining an appearance of the Al” phase in shape is called an [Al phase] in the present specification. The [Al phase] can be clearly distinguished from the Al phase that forms the above-described ternary eutectic structure in observation with a microscope.

[0030]

Also, the [Zn Phase] refers to a phase that is visible in an island shape with a clear boundary in the base of the above-described ternary eutectic structure, and a small amount of Al and furthermore a small amount of Mg may be actually dissolved therein. As far as viewed from the phase diagram, it is thought that other additive elements are not dissolved in the phase or the amount is extremely small even if they are dissolved. The [Zn phase] can be clearly distinguished from the Zn phase that forms the above-described ternary eutectic structure in observation with a microscope. The Zn-based plated layer of the present invention may contain the [Zn phase] depending on manufacturing conditions, but since almost no effect on improvement of corrosion resistance of a processed portion has been found in the experiment, there is no particular problem even if the [Zn phase] is contained in the plated layer.

[0031]

Also, the [MgZn₂ phase] refers to a phase that is visible in an island shape with a clear boundary in the base of the above-described ternary eutectic structure, and may actually contain a small amount of Al dissolved therein. As far as viewed from the phase diagram, it is thought that other additive elements are not dissolved in the phase or the amount is extremely small even if they are dissolved. The [MgZn₂ phase] can be clearly

distinguished from the MgZn_2 phase that forms the above-described ternary eutectic structure in observation with a microscope. The Zn-based plated layer of the present invention may not contain the $[\text{MgZn}_2 \text{ phase}]$ in some cases depending on manufacturing conditions, but the $[\text{MgZn}_2 \text{ phase}]$ is contained in the Zn-based plated layer under most of manufacturing conditions.

[0032]

Also, the $[\text{Mg}_2\text{Si phase}]$ refers to a phase that is visible in an island shape with a clear boundary in a solidified structure of the Zn-based plated layer when Si is added. As far as viewed from the phase diagram, it is thought that Zn, Al, and other additive elements are not dissolved or the amount is extremely small even if they are dissolved. The $[\text{Mg}_2\text{Si phase}]$ can be clearly distinguished in the Zn-based plated layer in observation with a microscope.

[0033]

Further, it is preferable that a surface of the Zn-based plated layer has any one element of Co, Fe, and Ni. Co, Fe, and Ni are attached 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. When these elements are present on the surface of the Zn-based plated layer, blackening resistance can be improved.

[0034]

Also, an arithmetic average roughness Ra on the surface of the Zn-based plated layer is preferably 0.1 to 2.0 μm . Also, the arithmetic average roughness Ra may be 0.5 to 2.0 μm . If Ra is 2.0 μm or less, metallic luster

of the Zn-based plated layer is improved to take on a more beautiful gold color. Also, since the effect may be saturated even if Ra is less than 0.1 μm, a lower limit may be set to 0.1 μm or more. The arithmetic average roughness Ra of the Zn-based plated layer is measured and calculated by a 3D laser microscope (manufactured by Keyence Co., Ltd.). A height Z is measured at a measurement interval of 50 μm using a standard lens with a magnification of 20 times. It is preferable that the number of measurement points be 100 points. With the number of measurement points being 100, the obtained height Z100 points are used from a height Z1 to a height Z100 to calculate the arithmetic average roughness Ra from the following Expression 3. Zave is an average of the height Z100 points.

$$Ra = 1/100 \times \sum [x = 1 \rightarrow 100] (|Height Zx - Zave|) \cdots \text{Expression 3}$$

[0035]

[Chemical conversion treatment layer]

Next, a chemical conversion treatment layer will be described. The chemical conversion treatment layer of the present embodiment contains a resin and a yellow colorant. The chemical conversion treatment layer of the present embodiment is a film obtained by applying an aqueous composition containing a resin and a yellow colorant to a Zn-based plated layer formed on the steel sheet and drying it.

[0036]

(Resin)

The resin contained in the chemical conversion treatment layer is preferably made of one or more of 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 originally water-insoluble but can be in a finely dispersed state in water such as emulsions or suspensions.

[0037]

The polyolefin resin is not particularly limited, and those obtained by radically polymerizing, for example, ethylene and unsaturated carboxylic acids such as methacrylic acid, acrylic acid, maleic acid, fumaric acid, itaconic acid, and crotonic acid under high temperature and high pressure conditions, then neutralizing it with ammonia or amine compounds, metal compounds such as KOH, NaOH, and LiOH, ammonia or amine compounds containing the above-described metal compounds, or the like, and dispersing it in water can be exemplified.

[0038]

The fluorine resin is not particularly limited, and, for example, a homopolymer or a copolymer of fluoroolefin can be mentioned. In a case of a copolymer, a copolymer of fluoroolefin, a fluorine-containing monomer other than fluoroolefin, and/or a monomer having no fluorine atom can be exemplified.

[0039]

The acrylic resin is not particularly limited, and those obtained by radically polymerizing, for example, unsaturated monomers such as styrene, alkyl (meta) acrylate, (meta) acrylic acid, hydroxyalkyl (meta) acrylates, and alkoxysilane (meta) acrylates in an aqueous solution using a polymerization initiator can be exemplified. The above-described polymerization initiator is not particularly limited, and, for example,

persulfates such as potassium persulfate and ammonium persulfate, azo compounds such as azobiscyanovaleric acid and azobisisobutyronitrile, and the like can be used.

[0040]

The urethane resin is not particularly limited, and those obtained by reacting, for example, 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, and tolylene diisocyanate, then extending the chain with a diamine or the like, and dispersing it in water, and the like can be mentioned.

[0041]

The polyester resin is not particularly limited, and those obtained by performing dehydration condensation of, for example, polyhydric alcohols such as ethylene glycol, propylene glycol, 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 hemic anhydride, neutralizing it with ammonia or amine compounds, and dispersing it in water can be exemplified.

[0042]

The epoxy resin is not particularly limited, and those obtained by reacting, for example, epoxy resins such as bisphenol A type epoxy resin,

bisphenol F type epoxy resin, resorcinol type epoxy resin, hydrogenated bisphenol A type epoxy resin, hydrogenated bisphenol F type epoxy resin, resorcinol type epoxy resin, and novolac type epoxy resin with amine compounds such as diethanolamine and N-methylethanolamine, and neutralizing it with an organic or inorganic acid, or those obtained by radically polymerizing a high acid value acrylic resin in the presence of the above-described epoxy resin, then neutralizing it with ammonia, an amine compound, or the like, and dispersing it in water can be mentioned.

[0043]

The phenol resin is not particularly limited, and those obtained by reacting, for example, phenolic resins such as methylolated phenolic resin obtained by addition reaction of aromatics such as phenol, resorcin, cresol, bisphenol A, and paraxylylene dimethyl ether, and formaldehyde in the presence of a reaction catalyst with amine compounds such as diethanolamine and N-methylethanolamine, and neutralizing it with an organic or inorganic acid can be exemplified.

[0044]

The resin is preferably contained in a proportion of 20% by mass or more in the chemical conversion treatment layer. When a resin content is set to be 20% by mass or more, the chemical conversion treatment layer itself does not become brittle and the Zn-based plated layer can be stably coated. Further, the chemical conversion treatment layer may contain components other than the resin such as silica particles, Nb compounds, and phosphate compounds along with the resin and the yellow colorant, and the resin content may be the balance of these components. Also, there is an

advantage in that corrosion resistance is secured when the resin content is 99.9% by mass or less.

[0045]

(Yellow colorant)

The chemical conversion treatment layer contains a yellow colorant. When a yellow colorant is contained in the chemical conversion treatment layer, the chemical conversion treatment layer is colored yellow, and, together with metallic luster of the Zn-based plated layer, an appearance of the Zn-based plated layer exhibits gold. In order to obtain this effect, a yellow colorant content in the chemical conversion treatment layer is preferably set in a range of 0.1 to 10% by mass. When the yellow colorant content in the chemical conversion treatment layer is set to be 0.1% by mass or more, the appearance of the Zn-based plated layer can be golden in color. Also, when the yellow colorant content is set to be 10% by mass or less, metallic luster of the Zn-based plated layer is not shielded and a gold color can be exhibited. Here, the appearance in the present invention means an appearance of the Zn-based plated steel sheet when viewed from a side of the Zn-based plated layer disposed on at least one side of the steel sheet.

[0046]

As the yellow colorant, a yellow pigment is preferable. A yellow pigment is excellent in weather resistance compared to a yellow dye. Also, when the chemical conversion treatment layer is formed, the chemical conversion treatment layer may be cooled with water, but a yellow dye may be eluted from the chemical conversion treatment layer into the cooling water, and thus a yellow pigment in which there is no likelihood of elution

is preferable. As the yellow pigment, an iron oxide-based yellow pigment or an azo-based yellow pigment is preferable. These pigments are preferable because they have a better weather resistance.

[0047]

As the yellow pigment, generally known ones can be used, and for example, an iron oxide-based yellow pigment or the like can be exemplified. As the iron oxide-based yellow pigment, generally known ones such as Pigment Yellow 42 can be used, and for example, iron oxide pigments sold by Lanxess Corporation, Ferro Corporation, Dainichiseika Color & Chemicals Mfg. Co., Ltd., or the like can be used. Also, chrome yellow or the like may be used as the yellow colorant. Also, as the azo-based yellow pigment, an acetoacetic arylide-based monoazo pigment, an acetoacetic arylide-based disazo pigment, a condensed azo pigment, a benzimidazolone-based monoazo pigment, or the like may be used.

[0048]

If a pigment in the chemical conversion treatment layer is an iron oxide-based yellow pigment, the content is measured by the following method. First, a thin film sample of the chemical conversion treatment layer is prepared by a microtome method so that a cross section perpendicular to a rolling direction of the Zn-based plated steel sheet of the present embodiment can be observed. In a region of $20\ \mu\text{m} \times t\ \mu\text{m}$ (a region with $20\ \mu\text{m}$ in a direction parallel to a sheet width direction and a film thickness of $t\ \mu\text{m}$ in a sheet thickness direction) of the obtained thin film sample, at least five regions are observed at a magnification of 100,000 times using a 200 kV field emission transmission electron microscope (FE-

TEM), and elemental mapping is performed using an energy dispersive X-ray spectrometer (EDS or EDX). An area ratio of the region in which Fe is present is obtained from the element mapping result. Here, using the same method as the above, an area ratio of a region in which Fe is present in each of a plurality of comparative samples having a chemical conversion treatment layer with a known pigment content is obtained, and a calibration curve is prepared in advance from a relationship with the pigment content. Using the calibration curve, a pigment content of a target sample is obtained.

[0049]

(Metal oxide particles)

Here, the yellow colorant colors the chemical conversion treatment layer yellow so that the appearance of the Zn-based plated layer is golden in color, but if the chemical conversion treatment layer contains a yellow colorant, corrosion resistance of the chemical conversion treatment layer may deteriorate. Therefore, in order to prevent deterioration in corrosion resistance of the chemical conversion treatment layer, metal oxide particles may be contained in the chemical conversion treatment layer of the present embodiment. As the metal oxide particles, an average particle size in a range of 5 to 200 nm is preferable. Since obtaining metal oxide particles having an average particle size of less than 5 nm itself is difficult, and preparing and manufacturing a chemical conversion treatment layer containing metal oxide particles having an average particle size of less than 5 nm are practically difficult, a lower limit of the average particle size of the metal oxide particles is set to 5 nm or more. Also, when the average

particle size of the metal oxide particles is 200 nm or less, the chemical conversion treatment layer does not become white turbidity, and a metal appearance of the Zn-based plated layer is not impaired. When metal oxide particles with an appropriate average particle size are contained, since light is slightly diffusely reflected inside the chemical conversion treatment layer, variations in light reflection can be suppressed by an effect of making minute scratches on the plated surface less noticeable visually or the like, and a sense of luxury can be given to the gold color. Therefore, an average particle size of the metal oxide particles is more preferably 5 to 50 nm.

[0050]

From the reason that the metal oxide particles appropriately control diffuse reflection of light inside the chemical conversion treatment layer, a refractive index thereof is preferably 1.3 to 2.5. The refractive index is measured by isolating the metal oxide particles from the chemical conversion treatment layer and using a commercially available refractive index measurement device.

[0051]

It is preferable that the metal oxide particles be contained in the chemical conversion treatment layer in a proportion of 1 to 20% by mass. When a metal oxide particle content is 1% by mass or more, an effect of improving corrosion resistance can be obtained. Also, when a metal oxide particle content is 20% by mass or less, the chemical conversion treatment layer itself does not become brittle and the Zn-based plated layer can be stably coated. It is more preferable that the metal oxide particle content be 3 to 7% by mass in the chemical conversion treatment layer from the

perspective of appropriately controlling diffuse reflection of light.

[0052]

Generally, since inorganic pigments such as metal oxide particles have a small particle size, the inorganic pigments may be present in the chemical conversion treatment layer in a form of secondary particles having a particle size larger than that of primary particles. The particle size of the secondary particles (particles in which inorganic pigments are aggregated) is described as “secondary particle size” below. In the metal oxide particles in the present embodiment, the primary particles and the secondary particles may be mixed, and even if the primary particles and the secondary particles are mixed, an average particle size may be in a range of 5 to 200 nm.

[0053]

The average particle size of metal oxide particles in the chemical conversion treatment layer is measured by the following method. First, a thin film sample of the chemical conversion treatment layer is prepared by a microtome method so that a cross section perpendicular to a rolling direction of the steel sheet of the present invention can be observed. In a region of $20\ \mu\text{m} \times t\ \mu\text{m}$ (a region with $20\ \mu\text{m}$ in a direction parallel to a plate width direction and a film thickness of $t\ \mu\text{m}$ in a plate thickness direction) of the obtained thin film sample, at least five regions are observed at a magnification of 100,000 times using a 200 kV field emission transmission electron microscope (FE-TEM). Using the following Expression 4, an equivalent circle diameter for all silica particles in the observation region is calculated, the equivalent circle diameter is used as a

particle size of each metal oxide particles, and an average particle size is obtained by averaging.

[0054]

Equivalent circle diameter = $2\sqrt{(s/\pi)}$... Expression 4

This is provided that, S is an area of metal oxide particles, and π is pi.

[0055]

The metal oxide particle content in the chemical conversion treatment layer is measured by the following method. First, separately from the target sample, a plurality of comparative samples having a chemical conversion treatment layer with a known metal oxide particle content are prepared, surfaces of these are measured with an X-ray fluorescence device, and a calibration curve is drawn from a relationship between an obtained detection intensity of the metal element and the metal oxide particle content. Next, the target sample is measured with the X-ray fluorescence device under the same conditions as the comparative samples, and the metal oxide particle content is obtained from the detection intensity of the metal element using the above-described calibration curve.

[0056]

Also, in the present invention, since an average particle size in a water-dispersed metal oxide particle state before being dispersed in a paint is also maintained in the chemical conversion treatment layer, that value may be used as the average particle size.

[0057]

It is preferable to optimize a mixing ratio of the metal oxide

particles and the yellow colorant. That is, the mixing ratio of the metal oxide particles and the yellow colorant ((metal oxide particles/yellow colorant) in a mass ratio) in the chemical conversion treatment layer is preferably in a range of 1 to 200. When the mixing ratio is set to 1 or more, corrosion resistance of the chemical conversion treatment layer can be improved even if the chemical conversion treatment layer contains a yellow colorant. Also, when the mixing ratio is set to 200 or less, deterioration of the appearance of the Zn-based plated layer can be prevented.

[0058]

It is more preferable that the metal oxide particles contain silica particles from the perspective of securing a balance between corrosion resistance and a golden appearance with a sense of luxury. Also, as the metal oxide particles, titania particles, alumina particles, zirconia particles, or the like having the same effect as the silica particles may be contained.

[0059]

The chemical conversion treatment layer may further contain either one or both of a Nb compound and a phosphate compound. When a Nb compound and a phosphate compound are contained, corrosion resistance of the Zn-based plated layer is improved.

[0060]

As the Nb compound, conventionally known niobium-containing compounds can be used, and for example, niobium oxide, niobic acid and salts thereof, fluoroniobate, fluorooxoniobate, and the like can be mentioned. Of these, niobium oxide is preferably used from the perspective of improving corrosion resistance.

[0061]

As the phosphate compounds, for example, 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), and diethylenetriaminepenta(methylenephosphonic acid), and salts thereof; organic phosphoric acids such as phytic acid and salts thereof; and the like can be mentioned. As a cationic species of salts is not particularly limited, and for example, Cu, Co, Fe, Mn, Sn, V, Mg, Ba, Al, Ca, Sr, Nb, Y, Ni, Zn, and the like can be mentioned. These may each be used alone or may be used in combination of two or more.

[0062]

The Nb compound and the phosphate compound are preferably contained in the chemical conversion treatment layer in a proportion of 0.5 to 30% by mass in total. If an amount of the Nb compound and the phosphate compound is 0.5% by mass or more, an effect of improving corrosion resistance can be obtained, and if an amount of the Nb compound and the phosphate compound is 30% by mass or less, the chemical conversion treatment layer does not become brittle and the Zn-based plated layer can be stably coated.

[0063]

Further, an adhesion amount of the chemical conversion treatment layer per side of the Zn-based plated layer is 0.1 to 15 g/m². If the adhesion amount is 0.1 g/m² or more, the adhesion amount of the chemical

conversion treatment layer is sufficient, the appearance of the Zn-based plated layer can be golden, and furthermore, corrosion resistance of the Zn-based plated layer can be improved. Also, if the adhesion amount is 15 g/m² or less, even if the chemical conversion treatment layer contains a yellow colorant, light reflection on the surface of the chemical conversion treatment layer is reduced, metallic luster of the surface of the Zn-based plated layer is not shielded, and the appearance of the Zn-based plated layer can be gold in color. A more preferable adhesion amount is 0.2 to 2g/m². Also, it is more preferable that a thickness of the chemical conversion treatment layer be 0.07 to 15 μm corresponding to the adhesion amount described above.

[0064]

The chemical conversion treatment layer may further contain at least one cross-linker selected from the group consisting of silane coupling agents, cross-linkable zirconium compounds, and cross-linkable titanium compounds. These may each be used alone or may be used in combination of two or more.

[0065]

If at least one cross-linker selected from the group consisting of silane coupling agents, cross-linkable zirconium compounds, and cross-linkable titanium compounds described above is contained, adhesion between the Zn-based plated layer and the chemical conversion treatment layer is further enhanced.

[0066]

The silane coupling agent described above is not particularly

limited, and examples thereof can 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, γ -mercaptopropyltrimethoxysilane, and the like. The silane coupling agents described above may each be used alone or may be used in combination of two or more.

[0067]

The cross-linkable zirconium compound described above 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 a compound soluble in water or an organic solvent is preferable, and a water-soluble zirconium compound is more preferable. As such a compound, zirconyl ammonium carbonate can be exemplified.

[0068]

The cross-linkable titanium compound described above 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 can include dipropoxy·bis(triethanolamine)titanium, dipropoxy·bis(diethanolamine)titanium, propoxy·tris(diethanolamine)titanium, dibutoxy·bis(triethanolamine)titanium, dibutoxy·bis(diethanolamine)titanium, dipropoxy·bis(acetylacetonato) titanium, dibutoxy·bis(acetylacetonato) titanium, dihydroxy·bis(lactato)titanium monoammonium salt, dihydroxy·bis(lactato)titanium diammonium salt, propanedioxytitanium bis(ethylacetoacetate), oxotitanium bis(monoammonium oxalate), isopropyl tri(N-amidoethyl·aminoethyl)titanate, and the like. The cross-linkers described above may each be used alone, or may be used in combination of two or more.

[0069]

At least one cross-linker selected from the group consisting of the silane coupling agent, cross-linkable zirconium compound, and cross-linkable titanium compound described above is preferably contained in an amount of 0.1 to 50% by mass with respect to 100% by mass of a solid content of the resin. If the cross-linker content is less than 0.1% by mass, an effect of improving adhesion may not be obtained, and if the cross-linker content exceeds 50% by mass, stability of the aqueous composition may be deteriorated.

[0070]

The chemical conversion treatment layer may further contain at least one cross-linker 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-linkers may each be used alone, or may be used in combination of two or more.

[0071]

When at least one cross-linker selected from the group consisting of the amino resin, the polyisocyanate compound, the block body thereof, the epoxy compound, and the carbodiimide compound described above is contained, a cross-link density is increased, barrier properties of the chemical conversion treatment layer are improved, and corrosion resistance is further improved.

[0072]

The amino resin described above is not particularly limited, and for example, a melamine resin, a benzoguanamine resin, a urea resin, a glycoluril resin, and the like can be mentioned.

[0073]

The polyisocyanate compound described above is not particularly limited, and for example, hexamethylene diisocyanate, isophorone diisocyanate, xylylene diisocyanate, tolylene diisocyanate, and the like can be mentioned. Also, blocked products thereof are a blocked product of the above-described polyisocyanate compound.

[0074]

The epoxy compound described above is not particularly limited as long as it is a compound having a plurality of oxirane rings, and for example, adipic acid diglycidyl ester, phthalate 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, and the like can be mentioned.

[0075]

As the carbodiimide compound, for example, a compound obtained by synthesizing an isocyanate-terminated polycarbodiimide by a condensation reaction accompanied by decarbonization of a diisocyanate compound such as an aromatic diisocyanate, an aliphatic diisocyanate, and an alicyclic diisocyanate, and then adding a hydrophilic segment having a functional group that has reactivity with an isocyanate group, and the like can be mentioned.

[0076]

At least one cross-linker selected from the group consisting of the amino resin, the polyisocyanate compound, the block body thereof, the epoxy compound, and the carbodiimide compound described above is preferably contained in an amount of 0.1 to 50% by mass with respect to 100% by mass of the solid content of the resin. If the content is less than 0.1% by mass, the content is small and an effect of improving corrosion resistance may not be obtained, and if the content exceeds 50% by mass, the chemical conversion treatment layer may become brittle and the corrosion resistance may deteriorate.

[0077]

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

[0078]

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

[0079]

The vanadium compound described above is not particularly limited, conventionally known vanadium-containing compounds can be used, and for example, vanadium acid, vanadate such as ammonium vanadate and sodium vanadate, phospho-vanadic acid, and phosphovanadates such as ammonium phosphovanadate, and the like can be mentioned.

[0080]

The tungsten compound described above is not particularly limited, conventionally known tungsten-containing compounds can be used, and for example, tungstate such as tungstic acid and ammonium tungstate, and sodium tungstate, phospho-tungstic acid, and phosphotungstates such as ammonium phosphotungstate, and the like can be mentioned.

[0081]

The molybdenum compound described above is not particularly limited, conventionally known molybdenum-containing compounds can be

used, and for example, molybdate and the like can be used. The molybdate described above is not limited in its framework and a degree of condensation, and for example, ortho-molybdate, paramolybdate, metamolybdate, and the like can be mentioned. Also, all salts such as simple salts and double salts are included, and examples of the double salts can include molybdate phosphate and the like.

[0082]

At least one selected from the group consisting of the vanadium compound, the tungsten compound and the molybdenum compound described above is preferably contained in an amount of 0.01 to 20% by mass with respect to 100% by mass of the solid content of the resin. If the amount of at least one selected from the group consisting of the vanadium compound, the tungsten compound and the molybdenum compound described above is less than 0.01% by mass, an effect of improving corrosion resistance may not be obtained, and if the amount of at least one selected from the group consisting of the vanadium compound, the tungsten compound, and the molybdenum compound described above exceeds 20% by mass, the chemical conversion treatment layer may become brittle and the corrosion resistance may deteriorate.

[0083]

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

[0084]

When the polyphenol compound is contained, corrosion resistance of the chemical conversion treatment layer and adhesion of a post-coating film

when used for post-coating applications or the like are improved.

[0085]

The polyphenol compound described above is a compound having two or more phenolic hydroxyls bonded to a benzene ring, or a condensate thereof. As the above-described compound having two or more phenolic hydroxyls bonded to the benzene ring, for example, gallic acid, pyrogallol, catechol, and the like can be mentioned. The condensate of the compound having two or more phenolic hydroxyls bonded to a benzene ring is not particularly limited, and examples thereof can include a polyphenol compound that is widely distributed in the plant world, usually called tannic acid, and the like. Tannic acid is a generic term for aromatic compounds with a complex structure having a large number of phenolic hydroxyls that are widely distributed in the plant world. The tannic acid described above may be hydrolyzable tannic acid or condensed type tannic acid. The above-described tannic acid is not particularly limited, and examples thereof can include hamameli tannin, persimmon tannin, tea tannin, Chinese gall tannin, gallnut tannin, myrobalan tannin, dividivi tannin, algarovilla tannin, valonea tannin, catechin tannin, and the like.

[0086]

As the tannic acid, commercially available ones such as, for example, "Tannic acid extract A," "B tannic acid," "N tannic acid," "Industrial tannic acid," "purified tannic acid," "Hi tannic acid," "F tannic acid," "JP tannic acid" (all manufactured by Dainippon Pharmaceutical Co., Ltd.), and "Tannic acid: AL" (manufactured by Fuji Chemical Industries Co., Ltd.) can be used. The polyphenol compounds described above may

each be used alone, or may be used in combination of two or more.

[0087]

The polyphenol compound described above is preferably contained in an amount of 0.1 to 50% by mass with respect to 100% by mass of the solid content of the resin. If the polyphenol compound content is less than 0.1% by mass, an effect of improving corrosion resistance may not be obtained, and if the polyphenol compound content exceeds 50% by mass, stability of the aqueous composition may be deteriorated.

[0088]

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

[0089]

When the solid lubricant described above is contained, it is effective in improving lubricity of the chemical conversion treatment layer, workability during press forming, preventing scratches due to dies, handling, or the like, and preventing abrasion flaws during transportation of formed products and coils.

[0090]

The solid lubricant described above is not particularly limited, and known lubricants such as fluorine-based lubricants, hydrocarbon-based lubricants, fatty acid amide-based lubricants, ester-based lubricants, alcohol-based lubricants, metal soap-based lubricants, and inorganic-based lubricants can be exemplified. As a criterion for selecting a lubricant additive for improving workability, it is necessary to select a material such that the added lubricant is present on the surface of the chemical conversion

treatment layer rather than being dispersedly present in a formed chemical conversion treatment layer from the point of exhibiting a lubrication effect to the maximum by reducing friction between a surface of the formed workpiece and the die. That is, when the lubricant is dispersedly present in the formed chemical conversion treatment layer, a coefficient of surface friction is high, the chemical conversion treatment layer is likely to be destroyed, and powdery materials are peeled off and deposited, resulting in poor appearance that is called a powdering phenomenon and deterioration of workability. As the material that is present on the surface of the chemical conversion treatment layer, a material that is not compatible with the resin and has a low surface energy is selected.

[0091]

The solid lubricant described above is preferably contained in an amount of 0.1 to 30% by mass with respect to 100% by mass of the solid content of the resin. If the solid lubricant content described above is less than 0.1%, an effect of improving workability is small, and if the solid lubricant content described above exceeds 30%, corrosion resistance may deteriorate.

[0092]

A coating method of an aqueous composition used for forming the chemical conversion treatment layer is to form a film by applying the aqueous composition to a surface of the Zn-based plated layer. The coating method is not particularly limited, and generally used methods such as roll coating, air spraying, airless spraying, immersion, and the like can be employed as appropriate. In order to enhance curing properties 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 the heat-drying method, any method such as hot air, induction heating, near-infrared, and far-infrared may be used, or these may be used in combination. A heating temperature of the object to be coated is 50 to 250°C, and preferably 70 to 220°C. If the heating temperature is lower than 50°C, since an evaporation rate of moisture is slow and film-forming properties cannot be sufficiently obtained, corrosion resistance may be deteriorated. On the other hand, if the heating temperature exceeds 250°C, thermal decomposition of the resin occurs, the corrosion resistance deteriorates, and an appearance deteriorates due to yellowing or the like. A drying time in a case of heat drying after coating is preferably 1 second to 5 minutes. Further, in a case of heat drying, water-cooling is preferable when it is manufactured in a continuous line from the perspective of productivity.

[0093]

An arithmetic average height S_a of the chemical conversion treatment layer is preferably 5 nm to 100 nm. When an arithmetic average height S_a of the chemical conversion treatment layer is 100 nm or less, a transmittance of the chemical conversion treatment layer can be maintained. On the other hand, when S_a exceeds 100 nm, there is a likelihood that the transmittance of the chemical conversion treatment layer will deteriorate. The arithmetic average height S_a of the chemical conversion treatment layer is measured and calculated by the following method. A surface of a sample cut into a predetermined size from a Zn-based plated steel sheet is deposited with gold to a thickness of 50 nm, and the sample deposited with gold is

embedded in a resin and polished so that a cross section of the sample in a plate thickness direction is exposed. The arithmetic average height S_a of the chemical conversion treatment layer is obtained by observing the cross section of the sample with a scanning electron microscope at a magnification of 5000 times, and calculating a roughness of the gold-deposited layer when it is observed from a direction perpendicular to the cross section. Since the gold deposition is performed to make a boundary between the chemical conversion treatment layer and the resin clear, and a thickness of the gold-deposited layer can be ignored compared to that of the chemical conversion treatment layer, an arithmetic average height of the gold-deposited layer can be substituted for the arithmetic average height S_a of the surface of the chemical conversion treatment layer.

[0094]

[Appearance]

Next, an appearance of the Zn-based plated steel sheet of the present embodiment will be described. When the appearance of the Zn-based plated steel sheet of the present embodiment is evaluated in the CIE1976 (L^* , a^* , b^*) color space, b^* is 2 or higher and 60 or lower and b^*/a^* is -3 or higher and 3 or lower, and the 60-degree mirror surface glossiness G_s (60°) defined by JIS Z 8741:1997 is 50 to 200. Also, in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters the surface at an angle of 120° from the surface and the

light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 , in a plane perpendicular to a surface of the chemical conversion treatment layer, when L^* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*1 and, in the plane, when L^* obtained when light enters the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L^*2 , L^*1 and L^*2 satisfy the following Expression 1.

$$10 \geq L^*1/L^*2 \geq 2 \cdots \text{Expression 1}$$

The reason for limitations of these will be described below.

[0095]

Unless predetermined b^* and b^*/a^* are satisfied, metallic luster of the Zn-based plated layer cannot be visually recognized, and the appearance of the Zn-based plated layer does not exhibit gold because light luminance increases as more light is reflected on the surface of the Zn-based plated layer, and if reflection thereof is low, reflection on the chemical conversion treatment layer increases. Therefore, in order to obtain a synergistic effect of the Zn-based plated layer exhibiting metallic luster and the chemical conversion treatment layer that has been colored yellow with a yellow colorant, it was found that b^* and b^*/a^* and the 60-degree mirror surface glossiness G_s (60°) need to be in a predetermined range, and L^*1 and L^*2 need to satisfy $10 \geq L^*1/L^*2 \geq 2$ (Expression 1).

[0096]

When b^* in a case of being evaluated in the CIE1976 (L^* , a^* , b^*)

color space is lower than 2, the color almost disappears and does not exhibit gold. Also, when b^* exceeds 60, it becomes a darker color, a metallic appearance is not sufficiently recognized, and a gold color is not exhibited. Therefore, b^* is set to in a range of 2 or higher and 60 or lower. A lower limit value of b^* is preferably 3.5, and more preferably 5, from the perspective of maintaining the gold color. An upper limit value of b^* is preferably 40, and more preferably 30, from the perspective of maintaining the metallic appearance.

[0097]

When b^*/a^* in a case of being evaluated in the CIE1976 (L^* , a^* , b^*) color space is lower than -3 , a yellowish red color becomes darker and a gold color is not exhibited. Also, when b^*/a^* exceeds 3, a green color becomes darker and a gold color is not exhibited. Therefore, b^*/a^* is set to in a range of -3 or higher and 3 or lower.

[0098]

Also, when the 60-degree mirror surface glossiness G_s (60°) is lower than 50, the appearance of the Zn-based plated steel sheet comes closer to white, the metallic luster of the Zn-based plated layer is impaired, and the appearance of the Zn-based plated layer does not exhibit gold. Also, when the 60-degree mirror surface glossiness G_s (60°) exceeds 200, reflection on the surface of the chemical conversion treatment layer becomes stronger, and the appearance of the Zn-based plated layer exhibits yellow and does not exhibit gold.

[0099]

Also, when L^*1/L^*2 is 10 or lower, there is an effect of producing

better gold color. When L^*1/L^*2 is 2 or higher, there is an effect of maintaining a metallic appearance. A lower limit value of L^*1/L^*2 is more preferably 4 from the perspective of maintaining a more beautiful metallic appearance. An upper limit value of L^*1/L^*2 is more preferably 7 from the perspective of producing a gold color with a sense of luxury.

[0100]

Also, as for the appearance of the Zn-based plated steel sheet of the present embodiment, when L^* in a range of 0.5 mm in diameter centered at each point is measured for arbitrary five points on the plated surface from which the surface layer coating film including the chemical conversion treatment layer has been removed, a maximum value of L^* ($L^*_{\max}$) is preferably 1.2 times or more a minimum value of L^* ($L^*_{\min}$).

[0101]

When the maximum value of L^* ($L^*_{\max}$) is 1.2 times or more the minimum value of L^* ($L^*_{\min}$), local fluctuations occur in a gold color, resulting in an effect of creating a deep sense of luxury.

[0102]

For the plated surface from which the surface layer coating film including the chemical conversion treatment layer has been removed with a coating remover (for example, a Neo rever SP-751 manufactured by Sansai Kako Co., Ltd.) that does not corrode the plating, five arbitrarily selected points are measured for L^* at each point using a Micro Spectrophotometer (VSS 7700, manufactured by Nippon Denshoku Industries Co., Ltd.). Of the measured L^* , the maximum one is defined as $L^*_{\max}$, and the minimum one is defined as $L^*_{\min}$.

[0103]

Also, a patterned portion disposed to have a predetermined shape and a non-patterned portion may be formed on the surface of the Zn-based plated layer according to the present embodiment.

It is preferable that the patterned portion be disposed to have a shape of any one of a linear portion, a curved portion, a dot portion, a figure, a numeral, a symbol, a pattern, and a letter, or a combination of two or more of these. Also, the non-patterned portion is a region other than the patterned portion. Also, even if a shape of the patterned portion is partially missing such as dot omission, it is permissible as long as the shape can be recognized as a whole. Also, the non-patterned portion may have a shape that borders a boundary of the patterned portion.

[0104]

When a shape of any one of a linear portion, a curved portion, a dot portion, a figure, a numeral, a symbol, a pattern, and a letter, or a combination of two or more of these is disposed on the surface of the Zn-based plated layer, these regions can be referred to as the patterned portion, and the other region can be referred to as the non-patterned portion. A boundary between the patterned portion and the non-patterned portion can be recognized with the naked eye. The boundary between the patterned portion and the non-patterned portion may be ascertained from an enlarged image using an optical microscope or a magnifying glass.

[0105]

The patterned portion may be formed to have a size to an extent in which the presence of the patterned portion is allowed to be determined with

the naked eye, a magnifying glass, or a microscope. Also, the non-patterned portion is a region that occupies most of the Zn-based plated layer (surface of the Zn-based plated layer), and the patterned portion may be disposed within the non-patterned portion.

The patterned portion is disposed in a predetermined shape within the non-patterned portion. Specifically, in the non-patterned portion, the patterned portion is disposed to have a shape of any one of a linear portion, a curved portion, a figure, a dot portion, a figure, a numeral, a symbol, a pattern, and a letter, or a combination of two or more of these. When the shape of the patterned portion is adjusted, a shape of any one of a linear portion, a curved portion, a figure, a dot portion, a figure, a numeral, a symbol, a pattern, and a letter, or a combination of two or more of these appears on the surface of the Zn-based plated layer. For example, a letter string, a number string, a symbol, a mark, a diagram, a design image, a combination of these, or the like formed of the patterned portion appears on the surface of the Zn-based plated layer. This shape is a shape intentionally or artificially formed by a manufacturing method to be described later, and is not a shape naturally formed.

[0106]

As described above, the patterned portion and the non-patterned portion are regions formed on the surface of the Zn-based plated layer, and the patterned portion and the non-patterned portion each include one or two of a first region and a second region.

[0107]

The patterned portion and the non-patterned portion each include

one or two of the first region and the second region determined by any of the following determination methods 1 to 5, and an absolute value of a difference between an area ratio of the first region in the patterned portion and an area ratio of the first region in the non-patterned portion is 30% or more. When an absolute value of the difference between the area ratio of the first region in the patterned portion and the area ratio of the first region in the non-patterned portion is 30% or more, the patterned portion and the non-patterned portion can be distinguished. When the difference in area ratio is less than 30%, the difference between the area ratio of the first region in the patterned portion and the area ratio of the first region in the non-patterned portion is small, and appearances of the patterned portion and the non-patterned portion are similar, making it difficult to identify the patterned portion. The larger the difference in area ratio, the better, the difference in area ratio is more preferably 40% or more, and the difference in area ratio is still more preferably 60% or more.

[0108]

That is, in the patterned portion, an area ratio of each of the first region and the second region can be obtained. When an area fraction of the first region exceeds 70%, the patterned portion appears relatively white or close to white compared to when the area fraction of the first region is 70% or less. When the area fraction of the first region is 30% or more and 70% or less, the patterned portion looks like a pear skin. Also, when the area fraction of the first region is less than 30%, the patterned portion appears to have metallic luster. As described above, an appearance of the patterned portion depends on the area fraction of the first region.

[0109]

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

[0110]

Then, when an absolute value of the difference between the area ratio of the first region in the patterned portion and the area ratio of the first region in the non-patterned portion is 30% or more, the patterned portion and the non-patterned portion can be distinguished. When the difference in area ratio is less than 30%, the difference between the area ratio of the first region in the patterned portion and the area ratio of the first region in the non-patterned portion is small, and appearances of the patterned portion and the non-patterned portion become similar, making it difficult to identify the patterned portion. The larger the difference in area ratio, the better, and the difference in area ratio is more preferably 40% or more and still more preferably 60% or more.

[0111]

[Determination method 1]

In determination method 1, virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, an inside of a circle with a diameter of 0.5 mm centered at a centroid point of each region of a plurality of regions partitioned by the virtual lattice lines is defined as a measurement region A, and an L^* value in each measurement region A is measured. When 50 points are selected arbitrarily from the obtained L^*

values and an average of the 50 points of the obtained L^* values is used as a reference L^* value, a region in which the L^* value is equal to or higher than the reference L^* value is defined as the first region, and a region in which the L^* value is lower than the reference L^* value is defined as the second region.

[0112]

[Determination method 2]

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

[0113]

[Determination method 3]

In determination method 3, virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, and an arithmetic average surface roughness S_a is measured in each of a plurality of regions partitioned by the virtual lattice lines. A region in which the obtained S_a is 1 μm or more is defined as a first region, and a region in which the obtained S_a is less than 1 μm is defined as a second region. The arithmetic average surface roughness S_a is measured using a 3D laser microscope (manufactured by Keyence Corporation). In the present

embodiment, a standard lens with a magnification of 20 times is used to measure a height Z in each of the plurality of regions partitioned by the virtual lattice lines at a measurement interval of 50 μm . When it is measured on a grid, 100 measurement points are obtained in the region. Using obtained height Z100 points from a height Z1 to a height Z100, the arithmetic average surface roughness Sa is calculated from the following Expression 5. Zave is an average of the height Z100 points.

$$Sa = 1/100 \times \sum_{x=1 \rightarrow 100} (|\text{Height } Z_x - Z_{ave}|) \cdots \text{Expression 5}$$

[0114]

[Determination method 4]

In determination method 4, virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a (0002) plane of the Zn phase and a diffraction peak intensity I_{10-11} of a (10-11) plane of the Zn phase are measured for each region by an X-ray diffraction method by which X-rays are incident on each of a plurality of regions partitioned by the virtual lattice lines, and a ratio of these intensities (I_{0002}/I_{10-11}) is defined as an orientation ratio. A region having the orientation ratio of 3.5 or more is defined as the first region, and a region having the orientation ratio of less than 3.5 is defined as the second region.

[0115]

[Determination method 5]

In determination method 5, virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 1 mm, and then 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 lattice 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 included inside the circle S is 10 mm. An average value of a maximum diameter $R_{\max}$ and a minimum diameter $R_{\min}$ of the diameters R of the circles S in the plurality of regions is defined as a reference diameter R_{ave} , a region having the circle S with the diameter R smaller than the reference diameter R_{ave} is defined as the first region, and a region having the circle S with the diameter R equal to or larger than the reference diameter R_{ave} is defined as the second region.

[0116]

Formation of the patterned portion and the non-patterned portion determined by determination method 1 or 2 is performed after the Zn-based plated layer is formed. The formation of the patterned portion and the non-patterned portion is performed by adhering an acid solution to the surface of the Zn-based plated layer at 60 to 200°C. More specifically, an acid solution may be prepared and adhered to the surface of the Zn-based plated layer by printing means. As a printing means, general printing methods such as printing methods using various plates (gravure printing, flexographic printing, offset printing, silk printing, and the like) and inkjet methods can be applied.

[0117]

At a portion to which an acid 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 as is plated. Thereby, an appearance of the portion to which the acid solution is adhered changes compared to a portion

to which the acid solution is not adhered. In this way, it is presumed that a difference between an area ratio of the first region in the patterned portion and an area ratio of the first region in the non-patterned portion becomes large, making it possible to distinguish between the patterned portion and the non-patterned portion.

[0118]

A range in which the acid solution is adhered may be a region corresponding to the patterned portion or a region corresponding to the non-patterned portion.

[0119]

As the acid solution, inorganic acids such as hydrochloric acid, nitric acid, and sulfuric acid are preferably used. Also, a concentration of the acid in the acid solution is desirably 0.1 to 10% by mass. A temperature of the steel sheet when the acid solution is adhered is 60 to 200°C, and preferably 50 to 80°C. Area fractions of the first region and the second region on the surface of the Zn-based plated layer at the portion to which the acid solution is adhered can be adjusted by adjusting a type and a concentration of the acid solution.

[0120]

If a surface temperature of the Zn-based plated layer when the acid solution is adhered is lower than 60°C, it is not preferable because it takes time to form the patterned portion or the non-patterned portion, and if a surface temperature of the Zn-based plated layer exceeds 200°C, it is not preferable because the acid solution quickly volatilizes, making it impossible to form the patterned portion or the non-patterned portion.

[0121]

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

[0122]

Next, formation of the patterned portion and the non-patterned portion determined by determination method 3 is performed after formation of the Zn-based plated layer. The formation of the patterned portion and the non-patterned portion is performed by pressing a roll having a partially increased surface roughness against the surface of the Zn-based plated layer to transfer a surface shape of the roll to the Zn-based plated layer. For example, in order to form the patterned portion on the surface of the Zn-based plated layer, a roughness of a portion of the roll surface corresponding to the patterned portion is made larger than those of the other portions, and thereby the patterned portion that includes a large number of the first regions having a large surface roughness can be formed. Also, conversely, it is possible to use a roll in which a roughness of the portion corresponding to the patterned portion is made smaller than those of the other portions. A roughness of the roll surface (arithmetic average surface roughness, S_a (μm)) is such that a range of the roughness at the portion in which the roughness is increased is 0.6 to 3.0 μm , and preferably 1.2 to 3.0 μm . A range of the roughness at the portion in which the roughness is lowered is preferably 0.05 to 1.0 μm , and preferably 0.05 to 0.8 μm . The transfer may be performed when a surface temperature of the Zn-based plated layer is in a range of 100 to 300°C. Also, a difference between the roughness at the portion in which the roughness is increased and the

roughness at the portion in which the roughness is lowered is set to more than $0.2\text{ }\mu\text{m}$ and preferably $0.3\text{ }\mu\text{m}$ or more in terms of the arithmetic average surface roughness S_a . As the difference in roughness decreases, it becomes difficult to distinguish between the patterned portion and the non-patterned portion.

[0123]

Formation of the patterned portion and the non-patterned portion determined by determination method 4 is performed on a steel sheet immediately after being pulled up from a hot-dip plating bath by locally spraying a non-oxidizing gas onto the metal in a molten state with a gas nozzle. Nitrogen or argon may be used as the non-oxidizing gas. Although an optimum temperature range differs according to a composition, it is preferable to spray the non-oxidizing gas when a temperature of the molten metal is in a range of (final solidification temperature -5) $^{\circ}\text{C}$ to (final solidification temperature $+5$) $^{\circ}\text{C}$. Further, a temperature of the non-oxidizing gas is set to lower than the final solidification temperature.

[0124]

When the Zn-based plated layer is in the above-described temperature range, a cooling rate of the molten metal increases at the portion in which the non-oxidizing gas has been sprayed, and thereby an orientation ratio of the Zn-based plated layer after solidification increases. On the other hand, a cooling rate of the molten metal is lowered at the portion in which the non-oxidizing gas has not been sprayed, and thereby an orientation ratio of the Zn-based plated layer after solidification is lowered. Therefore, when a range of spraying the non-oxidizing gas is adjusted, it is

possible to intentionally or arbitrarily adjust portions in which the region with a high orientation ratio and the region with a low orientation ratio appear.

[0125]

Thereby, shapes of the patterned portion and the non-patterned portion can be arbitrarily adjusted, and the patterned portion and the non-patterned portion can be distinguished. Since the orientation ratio becomes higher as the temperature of the sprayed gas becomes lower, the orientation ratio can be adjusted by the temperature of the sprayed gas. The temperature of the gas is preferably lower than the final solidification temperature, and may be adjusted to, for example, 25 to 250°C.

[0126]

Formation of the patterned portion and the non-patterned portion determined by determination method 5 is performed on a steel sheet immediately after being pulled up from a hot-dip plating bath by locally spraying a non-oxidizing gas having a final solidification temperature of the plating or higher onto the metal in a molten state with a gas nozzle. Nitrogen or argon may be used as the non-oxidizing gas. Although an optimum temperature range differs according to a composition, it is preferable to spray the non-oxidizing gas when a temperature of the molten metal is in a range of (final solidification temperature-5)°C to (final solidification temperature+5)°C. Further, a temperature of the non-oxidizing gas is preferably equal to or higher than the final solidification temperature. For example, in a plating composition with 11% of Al and 3% of Mg, it is preferable to spray a non-oxidizing gas having a gas

temperature equal to or higher than the final solidification temperature when a temperature of the molten metal is 330 to 340°C.

[0127]

A cooling rate of the molten metal is lowered in the vicinity in which the non-oxidizing gas is sprayed, and thereby boundaries appearing on the surface or crystal grain boundaries become coarse. Therefore, when a spray amount and a range of the non-oxidizing gas are adjusted, a size of boundaries appearing on the surface or crystal grain boundaries can be arbitrarily adjusted.

[0128]

When an absolute value of the difference between the area ratio of the first region in the patterned portion and the area ratio of the first region in the non-patterned portion is made to be 30% or more, the patterned portion and the non-patterned portion can be distinguished. The formed patterned portion and non-patterned portion are not formed by printing or painting, and thus have high durability. Also, since the patterned portion and the non-patterned portion are not formed by printing or painting, there is no influence on the corrosion resistance of the Zn-based plated layer. Therefore, the Zn-based plated steel sheet of the present embodiment has excellent corrosion resistance.

[0129]

In the Zn-based plated layer in which the patterned portion is formed, a Zn-based plated steel sheet having high durability of the patterned portion and suitable plating properties such as corrosion resistance can be provided. Since the patterned portion can be intentionally or artificially

shaped, the patterned portion can be disposed to have a shape of any one of a linear portion, a curved portion, a dot portion, a figure, a numeral, a symbol, a pattern, and a letter, or a combination of two or more of these. Thereby, various designs, trademarks, and other identification marks can be displayed on the surface of the Zn-based plated layer without printing or painting, and identifiability of the origin of the steel sheet and design quality can be improved. Also, information required for process control, inventory control, or the like and arbitrary information requested by a consumer can be given to the hot-dip plated steel sheet by the patterned portion. Thereby, this can also contribute to improving productivity of the Zn-based plated steel sheet.

Then, according to the Zn-based plated steel sheet of the present embodiment, since a chemical conversion treatment layer containing a yellow colorant is formed on the Zn-based plated layer in which the patterned portion is formed, visibility of the patterned portion can be further improved.

[Examples]

[0130]

The present invention will be specifically described below with reference to Examples.

[0131]

First, a cold-rolled steel sheet with a thickness of 1 mm was prepared, immersed in a plating bath of each composition, and a plating adhesion amount was adjusted to 80 g/m² on one side by N₂ wiping. Plating compositions of the obtained Zn-based plated steel sheets are shown

in Table 1.

[0132]

Also, when a patterned portion was formed on the Zn-based plated layer, the pattern was further formed by the following method. The patterned portion and the non-patterned portion each included one or two of the first region and the second region determined by any predetermined method of determination methods 1 to 5, and an absolute value of the difference between an area ratio of the first region in the patterned portion and an area ratio of the first region in the non-patterned portion was 40%.

[0133]

<Pattern 1>

A hydrochloric acid solution was adhered to a rubber plate having a protruding part or a recessed part with a square pattern of 50 mm on one side, and the rubber plate was pressed against a surface of the Zn-based plated layer to adhere an acid solution to the steel sheet, thereby forming a square patterned portion. A surface temperature of the Zn-based plated layer of the hot-dip plated steel sheet when the acid solution adhered was in a range of 60 to 200°C. Also, a portion other than the square patterned portion was defined as a non-patterned portion. Then, on the basis of determination method 2, virtual lattice lines were drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, an inside of a circle with a diameter of 0.5 mm centered at a centroid point of each region of a plurality of regions partitioned by the virtual lattice lines was defined as the measurement region A, the 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 designated as Example 59.

[0134]

<Pattern 2>

With a surface temperature of the Zn-based plated layer set to 100 to 300°C, a roll having a square pattern of 50 mm on one side was pressed against a surface of the Zn-based plated layer to form a patterned portion. A portion of the square pattern was defined as a patterned portion, and a portion other than the square pattern was defined as a non-patterned portion. On the basis of determination method 3, virtual lattice lines were drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, and the arithmetic average surface roughness S_a was measured in each of a plurality of regions partitioned by the virtual lattice lines. A region in which the obtained S_a was 1 μm or more was defined as a first region, and a region in which the obtained S_a was less than 1 μm was defined as a second region. This Zn-based plated steel sheet was designated as Example 60.

[0135]

<Pattern 3>

When the steel sheet was pulled up from the plating bath, nitrogen gas, which was a type of non-oxidizing gas, was sprayed onto a molten metal on the surface of the steel sheet with a gas nozzle when a temperature of the molten metal was in a range of (final solidification temperature-5)°C to (final solidification temperature+5)°C. A temperature of the gas was lower than the final solidification temperature. Thereafter, the molten

metal was cooled to be completely solidified. A range of spraying the nitrogen gas was controlled to be a square pattern of 50 mm on one side. A portion of the square pattern was defined as a patterned portion, and a portion other than the square pattern was defined as a non-patterned portion. On the basis of determination method 4, virtual lattice lines were drawn on the surface of the Zn-based plated layer at intervals of 1 mm or 10 mm, a diffraction peak intensity I_{0002} of a (0002) plane of the Zn phase and a diffraction peak intensity I_{10-11} of a (10-11) plane of the Zn phase were measured for each region by an X-ray diffraction method by which X-rays were incident on each of a plurality of regions partitioned by the virtual lattice lines, and a ratio of these intensities (I_{0002}/I_{10-11}) was defined as an orientation ratio. A region having the orientation ratio of 3.5 or more was defined as a first region, and a region having the orientation ratio of less than 3.5 was defined as a second region. This Zn-based plated steel sheet was designated as Example 61.

[0136]

<Pattern 4>

When the steel sheet was pulled up from the plating bath, nitrogen gas, which was a type of non-oxidizing gas, in a heated state was sprayed onto a molten metal on the surface of the steel sheet with a gas nozzle when a temperature of the molten metal was in a range of (final solidification temperature-5)°C to (final solidification temperature+5)°C. Conditions of spraying the nitrogen were as shown in Table 1. A temperature of the gas was equal to or higher than the final solidification temperature. Thereafter, the molten metal was cooled to be completely solidified. A

range of spraying the nitrogen gas was controlled to be a square pattern of 50 mm on one side. A portion of the square pattern was defined as a patterned portion, and a portion other than the square pattern was defined as a non-patterned portion. Then, on the basis of determination method 5, virtual lattice lines were drawn on the surface of the Zn-based plated layer at intervals of 1 mm, and then the circle S centered at the centroid point G of each region was drawn for each of a plurality of regions partitioned by the virtual lattice lines. The diameter R of the circle S was set so that a total length of surface boundary lines of the Zn-based plated layer included inside the circle S was 10 mm. An average value of the maximum diameter $R_{\max}$ and the minimum diameter $R_{\min}$ of the diameters R of the circles S in the plurality of regions was defined as the reference diameter R_{ave} , a region having the circle S with the diameter R smaller than the reference diameter R_{ave} was defined as a first region, and a region having the circle S with the diameter R equal to or larger than the reference diameter R_{ave} was defined as a second region. This Zn-based plated steel sheet was designated as Example 62.

[0137]

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

[0138]

Next, a chromate-free chemical conversion treatment layer was

formed by applying an aqueous composition containing various aqueous resins (a urethane resin, a polyester resin, an olefin resin, an epoxy resin, an acrylic resin, a phenol resin, a fluorine resin), metal oxide particles, niobium oxide, sodium phosphate, and yellow colorants (an azo-based yellow pigment, an iron oxide-based yellow pigment) onto the surface of the Zn-based plated layer of the manufactured Zn-based plated steel sheet using a bar coater to have a dry adhesion amount of 1.5 g/m^2 , drying it in a hot-air drying furnace at a reaching plate temperature of 150°C , and then cooling it with water. Amounts of niobium oxide and sodium phosphate were each 5%. Further, as the metal oxide particles, silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), and zirconia (ZrO_2) were used. Also, details of the yellow colorant are shown in Table 2. Compositions and the like of the chemical conversion treatment layer are shown in Tables 4A to 5B. In the column of “Nb oxide” in Tables 5A and 5B, a case of containing niobium oxide was indicated by “○,” and a case of not containing niobium oxide was indicated by “×”. Also, in the column of “Na phosphate,” a case of containing sodium phosphate was indicated by “○,” and a case of not containing sodium phosphate was indicated by “×”.

[0139]

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

Using a glossmeter, 60° glossiness (%) of a surface of the Zn plated layer was measured on the basis of the method specified in JIS Z 8741. When the glossiness was 50 to 200%, it was rated as “A,” and when it was less than 50%, it was rated as “B”. Results are shown in Tables 6A and 6B.

[0140]

(b^* value, b^*/a^*)

Using Spectrophotometer (SE6000 manufactured by Nippon Denshoku Industries Co., Ltd.), a surface of the Zn plated layer on which the chemical conversion treatment layer was formed was measured. A case in which b^* was 2 or higher and 60 or lower was rated as “A,” and a case in which b^* was lower than 2 or higher than 60 was rated as “B”. Further, a case in which b^*/a^* was -3 or higher and 3 or lower was rated as “A,” and a case in which b^*/a^* was lower than -10 or higher than -3 was rated as “B”. Results are shown in Tables 6A and 6B.

(L^*/L^{*2})

A case in which L^*/L^{*2} was 4 or higher and 7 or lower was rated as “A,” a case of 2 or higher and lower than 4 or higher than 7 and 10 or lower was rated as “B,” and a case of lower than 2 or higher than 10 was rated as “C”.

[0141]

(Corrosion resistance)

A salt water spray test (JIS Z 2371:2015) was performed on the Zn-based plated steel sheet. For a portion to which Erichsen processing has been subjected, a state of white rust generation after 24 hours of the test time was observed and was determined by the rating described below. A rating of 3 or higher was regarded as passing. Results are shown in Tables 6A and 6B.

[0142]

4: Less than 5% of white rust generation

3: 5% or more and less than 10% of white rust generation

2: 10% or more and less than 30% of white rust generation

1: 30% or more of white rust generation

[0143]

(Golden appearance)

The surface of the Zn-plated layer of the Zn-based plated steel sheet was shown to five panelists, and a golden appearance was determined from how it looked to them. The evaluation was determined by the rating described below, and a rating of 3 or higher was regarded as passing.

Results are shown in Tables 6A and 6B.

[0144]

5: Four or more out of five people could recognize it as a golden color, felt that there was no variation in light reflection, and felt a sense of luxury.

4: Four or more out of five people could recognize it as a golden color and felt that there was no variation in light reflection.

3: Three out of five people could recognize it as a golden color.

2: Two out of five people could recognize it as a golden color.

1: Not more than one out of five people could recognize it as a golden color.

[0145]

As shown in Tables 1 to 6B, the Zn-based plated steel sheets of examples 1 to 71 all had the chemical conversion treatment layer satisfying the range of the present invention, and the corrosion resistance and the golden appearance were satisfactory.

Also, in examples 59 to 62 in which the patterned portion was

formed in the plated layer, the corrosion resistance and the golden appearance were satisfactory, and visibility of the patterned portion was significantly improved. Further, an adhesion amount of the chemical conversion treatment layer was set in a range of 0.1 to 15.0 g/m² for some examples, and the results were satisfactory.

[0146]

On the other hand, as shown in Tables 1 to 6B, in comparative example 1, since a resin was not contained in the chemical conversion treatment layer, the chemical conversion treatment layer itself became very brittle, and various evaluation tests could not be performed.

In comparative example 2, since a yellow colorant was not contained in the chemical conversion treatment layer, the b* value and b*/a* were out of the range of the present invention, and the golden appearance was insufficient.

In comparative examples 3, 4, and 5, since the chemical conversion treatment layers respectively contained Cu phthalocyanine, Co phthalocyanine, and quinacridone which were not yellow colorants according to the present invention, that is, yellow colorants were not contained in comparative examples 3 to 5, at least one of the b* value and b*/a* was out of the range of the present invention, and the golden appearance was insufficient.

In comparative examples 6 and 7, since the adhesion amount of the chemical conversion treatment layer was outside the range of 0.1 to 15.0 g/m², the b* value or the 60-degree mirror surface glossiness G_s (60°) was out of the range of the present invention, L*1/L*2 was out of the range of

the present invention, and the golden appearance was insufficient.

[0147]

[Table 1]

	Average composition of plated layer (mass%) with balance of 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	0.0001	—	—	—
Plated layer 18	11	3	0.01	—	—	—
Plated layer 19	11	3	0.2	—	—	—
Plated layer 20	11	3	1	—	—	—
Plated layer 21	11	3	2	—	—	—
Plated layer 22	6	3	0.01	—	—	—
Plated layer 23	6	3	0.1	—	—	—
Plated layer 24	6	3	1	—	—	—
Plated layer 25	6	3	2	—	—	—
Plated layer 26	0.1	—	—	0.08	—	—
Plated layer 27	0.1	—	—	—	0.08	—
Plated layer 28	0.1	—	—	—	—	0.08

[0148]

[Table 2]

	Details
Condensed azo pigment	AF Yellow E-12 manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.
Iron oxide	NAF502 manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

Chrome yellow	Reagent manufactured by Kanto Chemical Co., INC.
<u>Cu phthalocyanine</u>	NAF1052 manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.
<u>Co phthalocyanine</u>	Manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd
<u>Quinacridone</u>	NAF1032 manufactured by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

[0149]

[Table 3A]

	Zn-based plated layer			
	Types of plated layer	Pattern	Surface metal of plated layer	Arithmetic average roughness Ra (μm)
Example 1	Plated layer 19	None	Co	0.8
Example 2	Plated layer 19	None	Co	0.8
Example 3	Plated layer 19	None	Co	0.8
Example 4	Plated layer 19	None	Co	0.8
Example 5	Plated layer 19	None	Co	0.8
Example 6	Plated layer 19	None	Co	0.8
Example 7	Plated layer 19	None	Co	0.8
Example 8	Plated layer 19	None	Co	0.8
Example 9	Plated layer 19	None	Co	0.8
Example 10	Plated layer 19	None	Co	0.8
Example 11	Plated layer 19	None	Co	0.8
Example 12	Plated layer 19	None	Co	0.8
Example 13	Plated layer 19	None	Co	0.8
Example 14	Plated layer 19	None	Co	0.8
Example 15	Plated layer 19	None	Co	0.8
Example 16	Plated layer 19	None	Co	0.8
Example 17	Plated layer 19	None	Co	0.8
Example 18	Plated layer 19	None	Co	0.8
Example 19	Plated layer 19	None	Co	0.8
Example 20	Plated layer 19	None	Co	0.8
Example 21	Plated layer 19	None	Co	0.8
Example 22	Plated layer 19	None	Co	0.8
Example 23	Plated layer 19	None	Co	0.8
Example 24	Plated layer 19	None	Co	0.5
Example 25	Plated layer 19	None	Co	2
Example 26	Plated layer 19	None	Co	2.5
Example 27	Plated layer 19	None	None	0.8
Example 28	Plated layer 19	None	Fe	0.8
Example 29	Plated layer 19	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

[0150]

[Table 3B]

	Zn-based plated layer			
	Types of plated layer	Pattern	Surface metal of plated layer	Arithmetic average roughness Ra (μm)
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
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 19	None	Co	0.8
Example 59	Plated layer 19	Pattern 1	Co	0.8
Example 60	Plated layer 19	Pattern 2	Co	0.8
Example 61	Plated layer 19	Pattern 3	Co	0.8
Example 62	Plated layer 19	Pattern 4	Co	0.8
Example 63	Plated layer 19	None	Co	0.8
Example 64	Plated layer 19	None	Co	0.8
Example 65	Plated layer 19	None	Co	0.8
Example 66	Plated layer 19	None	Co	0.8
Example 67	Plated layer 19	None	Co	0.8
Example 68	Plated layer 19	None	Co	0.8

Example 69	Plated layer 19	None	Co	0.8
Example 70	Plated layer 19	None	Co	0.8
Example 71	Plated layer 19	None	Co	0.8
Comparative example 1	Plated layer 19	None	Co	0.8
Comparative example 2	Plated layer 19	None	Co	0.8
Comparative example 3	Plated layer 19	None	Co	0.8
Comparative example 4	Plated layer 19	None	Co	0.8
Comparative example 5	Plated layer 19	None	Co	0.8
Comparative example 6	Plated layer 19	None	Co	0.8
Comparative example 7	Plated layer 19	None	Co	0.8

[0151]

[Table 4A]

	Chemical conversion treatment layer								
	Types of resin	Resin content	Types of metal oxide particle	Refractive index of metal oxide particle	Average particle size of metal oxide particle (nm)	Metal oxide particle (mass%)	Yellow colorant	Yellow colorant content (mass%)	Metal oxide particles/ yellow colorant
Example 1	Urethane resin	60%	Silica	1.4	12	5	Condensed azo pigment	1	5
Example 2	Urethane resin	60%	Silica	1.4	100	5	Condensed azo pigment	1	5
Example 3	Urethane resin	60%	Silica	1.4	200	5	Condensed azo pigment	1	5
Example 4	Urethane resin	60%	Silica	1.4	45	1	Condensed azo pigment	0.2	5
Example 5	Urethane resin	60%	Silica	1.4	45	20	Condensed azo pigment	0.1	200
Example 6	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 7	Urethane resin	60%	Silica	1.4	45	5	Iron oxide	1	5
Example 8	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	10	0.5
Example 9	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	5	1
Example 10	Urethane resin	60%	Silica	1.4	45	20	Condensed azo pigment	1	20

Example 11	Urethane resin	60%	Silica	1.4	45	20	Condensed azo pigment	0.0667	300
Example 12	Polyester resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 13	Epoxy resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 14	Phenol resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 15	Polyolefin resin (particle size 0.1 μm)	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 16	Fluorine resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 17	Acrylic resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 18	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 19	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 20	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 21	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 22	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 23	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 24	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 25	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5

Example 26	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
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[0152]

[Table 4B]

	Chemical conversion treatment layer								
	Types of resin	Resin content	Types of metal oxide particle	Refractive index of metal oxide particle	Average particle size of metal oxide particle (nm)	Metal oxide particle (mass%)	Yellow colorant	Yellow colorant content (mass%)	Metal oxide particles/ yellow colorant
Example 27	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 28	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 29	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 30	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 31	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 32	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 33	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 34	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 35	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5

Example 36	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 37	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 38	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 39	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 40	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 41	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 42	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 43	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 44	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 45	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 46	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 47	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 48	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 49	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 50	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 51	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5

Example 52	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
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[0153]

[Table 4C]

	Chemical conversion treatment layer								
	Types of resin	Resin content	Types of metal oxide particle	Refractive index of metal oxide particle	Average particle size of metal oxide particle (nm)	Metal oxide particle (mass%)	Yellow colorant	Yellow colorant content (mass%)	Metal oxide particles/ yellow colorant
Example 53	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 54	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 55	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 56	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 57	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 58	Urethane resin	60%	Silica	1.4	45	5	Chrome yellow	1	5
Example 59	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Example 60	Urethane resin	60%	Silica	1.4	45	1	Condensed azo pigment	0.2	5
Example 61	Urethane resin	60%	Silica	1.4	45	1	Condensed azo pigment	0.2	5

Example 62	Urethane resin	60%	Silica	1.4	45	1	Condensed azo pigment	0.2	5
Example 63	Urethane resin	60%	None	–	–	–	Condensed azo pigment	0.2	–
Example 64	Urethane resin	60%	Silica	1.4	450	5	Condensed azo pigment	1	5
Example 65	Urethane resin	60%	Silica	1.4	45	12	Condensed azo pigment	12	1
Example 66	Urethane resin	60%	Silica	1.55	45	5	Condensed azo pigment	1	5
Example 67	Urethane resin	60%	Titania	2.4	45	5	Condensed azo pigment	1	5
Example 68	Urethane resin	60%	Alumina	1.6	45	5	Condensed azo pigment	1	5
Example 69	Urethane resin	60%	Zirconia	2.0	45	5	Condensed azo pigment	1	5
Example 70	Urethane resin	60%	Silica	1.4	45	10	Condensed azo pigment	10	1
Example 71	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
Comparative example 1	<u>None</u>	=	Silica	1.4	45	5	Condensed azo pigment	1	5
Comparative example 2	Urethane resin	60%	Silica	1.4	45	5	<u>None</u>	–	–
Comparative example 3	Urethane resin	60%	Silica	1.4	45	5	<u>Cu</u> phthalocyanine	1	5
Comparative example 4	Urethane resin	60%	Silica	1.4	45	5	<u>Co</u> phthalocyanine	1	5
Comparative example 5	Urethane resin	60%	Silica	1.4	45	5	<u>Quinacridone</u>	1	5
Comparative example 6	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5

Comparative example 7	Urethane resin	60%	Silica	1.4	45	5	Condensed azo pigment	1	5
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Underlined portion indicates outside the range of the present invention.

[0154]

[Table 5A]

	Chemical conversion treatment layer			
	Nb oxide	Na phosphate	Arithmetic average height Sa (nm)	Adhesion amount of chemical conversion treatment layer (g/m ²)
Example 1	○	○	10	1.5
Example 2	○	○	10	1.5
Example 3	○	○	10	1.5
Example 4	○	○	10	1.5
Example 5	○	○	10	1.5
Example 6	○	○	10	1.5
Example 7	○	○	10	1.5
Example 8	○	○	10	1.5
Example 9	○	○	10	1.5
Example 10	○	○	10	1.5
Example 11	○	○	10	1.5
Example 12	○	○	10	1.5
Example 13	○	○	10	1.5
Example 14	○	○	10	1.5
Example 15	○	○	10	1.5
Example 16	○	○	10	1.5
Example 17	○	○	10	1.5
Example 18	None	○	10	1.5
Example 19	○	None	10	1.5
Example 20	None	None	10	1.5
Example 21	○	○	5	1.5
Example 22	○	○	20	1.5
Example 23	○	○	25	1.5
Example 24	○	○	10	1.5
Example 25	○	○	10	1.5
Example 26	○	○	10	1.5
Example 27	○	○	10	1.5
Example 28	○	○	10	1.5
Example 29	○	○	10	1.5
Example 30	○	○	10	1.5
Example 31	○	○	10	1.5
Example 32	○	○	10	1.5
Example 33	○	○	10	1.5
Example 34	○	○	10	1.5
Example 35	○	○	10	1.5
Example 36	○	○	10	1.5

Example 37	○	○	10	1.5
Example 38	○	○	10	1.5
Example 39	○	○	10	1.5

[0155]

[Table 5B]

	Chemical conversion treatment layer			
	Nb oxide	Na phosphate	Arithmetic average height Sa (nm)	Adhesion amount of chemical conversion treatment layer (g/m ²)
Example 40	○	○	10	1.5
Example 41	○	○	10	1.5
Example 42	○	○	10	1.5
Example 43	○	○	10	1.5
Example 44	○	○	10	1.5
Example 45	○	○	10	1.5
Example 46	○	○	10	1.5
Example 47	○	○	10	1.5
Example 48	○	○	10	1.5
Example 49	○	○	10	1.5
Example 50	○	○	10	1.5
Example 51	○	○	10	1.5
Example 52	○	○	10	1.5
Example 53	○	○	10	1.5
Example 54	○	○	10	1.5
Example 55	○	○	10	1.5
Example 56	○	○	10	1.5
Example 57	○	○	10	1.5
Example 58	○	○	10	1.5
Example 59	○	○	10	1.5
Example 60	○	○	10	1.5
Example 61	○	○	10	1.5
Example 62	○	○	10	1.5
Example 63	○	○	10	1.5
Example 64	○	○	10	1.5
Example 65	○	○	10	1.5
Example 66	○	○	10	1.5
Example 67	○	○	10	1.5
Example 68	○	○	10	1.5
Example 69	○	○	10	1.5
Example 70	○	○	10	0.1

Example 71	○	○	10	15.0
Comparative example 1	○	○	10	1.5
Comparative example 2	○	○	10	1.5
Comparative example 3	○	○	10	1.5
Comparative example 4	○	○	10	1.5
Comparative example 5	○	○	10	1.5
Comparative example 6	○	○	10	<u>16.0</u>
Comparative example 7	○	○	10	<u>0.05</u>

Underlined portion indicates outside the range of the present invention.

[0156]

[Table 6A]

					Evaluation	
	b*	b*/a*	60-degree mirror surface glossiness G _s (60°)	L*1/L*2	Corrosion resistance	Golden appearance
Example 1	A	A	A	A	4	5
Example 2	A	A	A	A	4	4
Example 3	A	A	A	A	4	4
Example 4	A	A	A	A	4	5
Example 5	A	A	A	A	4	5
Example 6	A	A	A	A	4	5
Example 7	A	A	A	A	4	5
Example 8	A	A	A	A	3	4
Example 9	A	A	A	A	4	5
Example 10	A	A	A	A	4	5
Example 11	A	A	A	B	4	3
Example 12	A	A	A	A	4	5
Example 13	A	A	A	A	4	5
Example 14	A	A	A	A	4	5
Example 15	A	A	A	A	4	5
Example 16	A	A	A	A	4	5
Example 17	A	A	A	A	4	5
Example 18	A	A	A	A	3	5

Example 19	A	A	A	A	3	5
Example 20	A	A	A	A	3	5
Example 21	A	A	A	A	4	5
Example 22	A	A	A	A	4	5
Example 23	A	A	A	B	4	3
Example 24	A	A	A	A	4	5
Example 25	A	A	A	A	4	5
Example 26	A	A	A	B	4	3
Example 27	A	A	A	A	4	5
Example 28	A	A	A	A	4	5
Example 29	A	A	A	A	4	5
Example 30	A	A	A	A	3	5
Example 31	A	A	A	A	3	5
Example 32	A	A	A	A	3	5
Example 33	A	A	A	A	3	5
Example 34	A	A	A	A	3	5
Example 35	A	A	A	A	3	5
Example 36	A	A	A	A	3	5
Example 37	A	A	A	A	4	5
Example 38	A	A	A	A	4	5
Example 39	A	A	A	A	4	5

[0157]

[Table 6B]

					Evaluation	
	b*	b*/a*	60-degree mirror surface glossiness G _s (60°)	L*1/L*2	Corrosion resistance	Golden appearance
Example 40	A	A	A	A	4	5
Example 41	A	A	A	A	3	5
Example 42	A	A	A	A	4	5
Example 43	A	A	A	A	4	5
Example 44	A	A	A	A	4	5
Example 45	A	A	A	A	3	5
Example 46	A	A	A	A	4	5
Example 47	A	A	A	A	4	5
Example 48	A	A	A	A	4	5
Example 49	A	A	A	A	4	5
Example 50	A	A	A	A	4	5
Example 51	A	A	A	A	4	5

Example 52	A	A	A	A	4	5
Example 53	A	A	A	A	4	5
Example 54	A	A	A	A	4	5
Example 55	A	A	A	A	3	5
Example 56	A	A	A	A	3	5
Example 57	A	A	A	A	3	5
Example 58	A	A	A	A	4	3
Example 59	A	A	A	A	4	5
Example 60	A	A	A	A	4	5
Example 61	A	A	A	A	4	5
Example 62	A	A	A	A	4	5
Example 63	A	A	A	B	3	3
Example 64	A	A	A	A	4	3
Example 65	A	A	A	B	4	3
Example 66	A	A	A	A	4	5
Example 67	A	A	A	A	4	5
Example 68	A	A	A	A	4	5
Example 69	A	A	A	A	4	5
Example 70	A	A	A	B	3	3
Example 71	A	A	A	B	4	3
Comparative example 1	A	A	A	<u>C</u>	Evaluation was not possible because chemical conversion treatment layer was brittle.	
Comparative example 2	<u>B</u>	<u>B</u>	A	A	4	1
Comparative example 3	<u>B</u>	<u>B</u>	A	A	4	1
Comparative example 4	<u>B</u>	<u>B</u>	A	A	4	1
Comparative example 5	<u>B</u>	<u>B</u>	A	A	4	1
Comparative example 6	A	A	<u>B</u>	<u>C</u>	4	1
Comparative example 7	<u>B</u>	A	A	<u>C</u>	1	2

Underlined portion indicates outside the range of the present invention.

[Industrial Applicability]

[0158]

According to the present invention, in Zn-based plated steel sheets

containing Al, a Zn-based plated steel sheet exhibiting a golden appearance with a sense of luxury and having improved corrosion resistance can be provided, and therefore the present invention has high industrial applicability.

[CLAIMS]

We claim:

1. A Zn-based plated steel sheet comprising:

a steel sheet;

a Zn-based plated layer disposed on at least one side of the steel sheet and containing 0.05 to 60% by mass of Al, and Zn; and

at least one layer of a chromate-free chemical conversion treatment layer disposed on the Zn-based plated layer with an adhesion amount per side of 0.1 to 15 g/m², wherein

the chemical conversion treatment layer contains a resin and a yellow colorant,

when an appearance is evaluated in a CIE 1976 (L*, a*, b*) color space, b* is 2 or higher and 60 or lower and b*/a* is -3 or higher and 3 or lower, and a 60-degree mirror surface glossiness G_s (60°) defined by JIS Z 8741:1997 is 50 to 200, and

in a plane perpendicular to a surface of the chemical conversion treatment layer, when L* obtained when light enters the surface at an angle of 60° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L*1 and, in the plane, when L* obtained when light enters the surface at an angle of 120° from the surface and the light reflected from the surface is received at an angle of 135° from the surface is defined as L*2, L*1 and L*2 satisfy the following Expression 1.

$$10 \geq L^*1/L^*2 \geq 2 \cdots \text{Expression 1}$$

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

yellow colorant is an azo-based yellow pigment or an iron oxide-based yellow pigment.

3. The Zn-based plated steel sheet according to claim 1 or 2, wherein an amount of the yellow colorant in the chemical conversion treatment layer is 0.1 to 10% by mass.

4. The Zn-based plated steel sheet according to any one of claims 1 to 3, wherein L^*1 and L^*2 satisfy the following Expression 2.

$$7 \geq L^*1/L^*2 \geq 4 \cdots \text{Expression 2}$$

5. The Zn-based plated steel sheet according to any one of claims 1 to 4, wherein the chemical conversion treatment layer contains 1 to 20% by mass of metal oxide particles having an average particle size of 5 to 200 nm and a refractive index of 1.3 to 2.5.

6. The Zn-based plated steel sheet according to claim 5, wherein the metal oxide particles include silica particles.

7. The Zn-based plated steel sheet according to claim 5 or 6, wherein a mixing ratio of the yellow colorant and the metal oxide particles in the chemical conversion treatment layer is in a range of 1 to 200.

8. The Zn-based plated steel sheet according to any one of claims 1 to 7, wherein an arithmetic average roughness Ra on a surface of the Zn-based plated layer is 0.1 to 2.0 μm .

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

10. The Zn-based plated steel sheet according to any one of claims 1 to 9,

wherein the chemical conversion treatment layer further contains either one or both of a Nb compound and a phosphate compound.

11. The Zn-based plated steel sheet according to any one of claims 1 to 10, wherein the resin in the chemical conversion treatment layer includes one or more of a polyolefin resin, a fluorine resin, an acrylic resin, a urethane resin, a polyester resin, an epoxy resin, and a phenol resin.

12. The Zn-based plated steel sheet according to any one of claims 1 to 11, wherein the Zn-based plated layer contains, in an average composition, 4% by mass or more and 22% by mass or less of Al, more than 1% by mass and 10% by mass or less of Mg, and a balance being Zn and impurities.

13. The Zn-based plated steel sheet according to any one of claims 1 to 12, wherein the Zn-based plated layer further contains, in an average composition, 0.0001 to 2% by mass of Si.

14. The Zn-based plated steel sheet according to any one of claims 1 to 13, wherein the Zn-based plated layer further contains, in an average composition, one or more of Ni, Sb, and Pb in an amount of 0.0001 to 2% by mass in total.

15. The Zn-based plated steel sheet according to any one of claims 1 to 14, wherein when L^* in a range of 0.5 mm in diameter centered at each point is measured for arbitrary five points on the plated surface, a maximum value of L^* is 1.2 times or more a minimum value of L^* .

16. The Zn-based plated steel sheet according to any one of claims 1 to 15, wherein

a patterned portion disposed to have a predetermined shape and a non-patterned portion are formed on the Zn-based plated layer,

the patterned portion and the non-patterned portion each include one or two of a first region and a second region determined by any of the following determination methods 1 to 5, and

an absolute value of a difference between an area ratio of the first region in the patterned portion and an area ratio of the first region in the non-patterned portion is 30% or more.

[Determination method 1]

Virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 0.5 mm, an inside of a circle with a diameter of 0.5 mm centered at a centroid point of each region of a plurality of regions partitioned by the virtual lattice lines is defined as a measurement region A, and an L^* value in each measurement region A is measured. When 50 points are selected arbitrarily from the obtained L^* values and an average of the 50 points of the obtained L^* values is used as a reference L^* value, a region in which the L^* value is equal to or higher than the reference L^* value is defined as the first region, and a region in which the L^* value is lower than the reference L^* value is defined as the second region.

[Determination method 2]

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

region.

[Determination method 3]

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

[Determination method 4]

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

[Determination method 5]

Virtual lattice lines are drawn on the surface of the Zn-based plated layer at intervals of 1 mm, and then 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 lattice 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 included

inside the circle S is 10 mm. An average value of a maximum diameter $R_{\max}$ and a minimum diameter $R_{\min}$ of the diameters R of the circles S in the plurality of regions is defined as a reference diameter R_{ave} , a region having the circle S with the diameter R smaller than the reference diameter R_{ave} is defined as the first region, and a region having the circle S with the diameter R equal to or larger than the reference diameter R_{ave} is defined as the second region.

17. The Zn-based plated steel sheet according to any one of claims 1 to 16, wherein the surface of the Zn-based plated layer contains any one of Co, Fe, and Ni.