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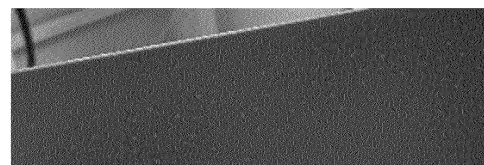
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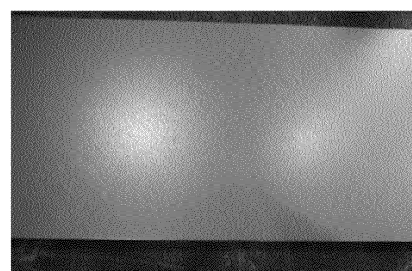
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(54) **SOLUTION COMPOSITION FOR STEEL SHEET SURFACE TREATMENT, STEEL SHEET SURFACE-TREATED USING SAME, AND MANUFACTURING METHOD THEREFOR**

(57) The present invention relates to a solution composition capable of improving pitting corrosion resistance and blackening resistance of a steel sheet, a steel sheet surface-treated using same, and a method for manufacturing the steel sheet.



(a)



(b)

FIG. 1

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Description

Technical Field

5 **[0001]** The present disclosure relates to a solution composition capable of improving pitting corrosion resistance and blackening resistance of a steel sheet, a steel sheet surface-treated using the same, and a manufacturing method for the steel sheet.

Background Art

10 **[0002]** A highly corrosion-resistant hot-dip galvanized steel material with a plating layer containing zinc (Zn), magnesium (Mg), and aluminum (Al) is known as a steel material having excellent red rust corrosion resistance.

[0003] However, most exposed surfaces of these highly corrosion-resistant hot-dip galvanized steel materials are formed of zinc or zinc alloy, so when exposed to a general environment, especially, a humid atmosphere, there may be a problem in that point-like corrosive defects may easily occur on the exposed surfaces to deteriorate the appearance thereof. In addition, recently, foreign material defects have occurred in which a coating layer of hot-dip galvanized steel material sticks to a roll as the hot-dip galvanized steel material passes through the roll in a toll processing process.

15 **[0004]** To solve the problem, in the related art, corrosion resistance and blackening resistance have been secured by performing hexavalent chromium or chromate treatment on plated steel sheets. However, as hexavalent chromium has been designated as a hazardous environmental substance, regulations on the use of hexavalent chromium have currently been strengthened. Moreover, when hexavalent chromium is used as a surface treatment agent for plated steel sheets, there is a problem of defects in which a surface of a steel sheet turns black or black spots occur.

[0005] Accordingly, a method of coating a plated steel sheet with a surface treatment solution composition containing trivalent chromium to secure corrosion resistance and blackening resistance of the plated steel sheet has been developed.

25 **[0006]** For example, Patent Document 1 applies a method of chemical conversion treatment by immersing a steel sheet in a composition containing trivalent chromium. This method has problems, in that an immersion time is relatively long to apply to a continuous process of steel companies and the chemical conversion treatment method impairs anti-fingerprint properties of the steel sheet.

[0007] Meanwhile, Patent Documents 2 and 3 disclose that a composition containing trivalent chromium is applied to a plated steel sheet using a spray or roll coater method, which may be applied to a continuous line of steel companies and ensure anti-fingerprint properties. However, these compositions contain porous silica components, and thus, are not suitable for Mg- and Al-based alloys, which are prone to severe discoloration in a humid atmosphere. In addition, porous silica has strong moisture absorption properties, which may cause rapid discoloration in Zn-Mg-Al-based alloy steel sheets.

35 [Related Art Document]

[0008]

40 (Patent Document 1) Korean Application Publication No. 10-2009-0024450
 (Patent Document 2) Korean Application Publication No. 10-2004-0046347
 (Patent Document 3) Japanese Application Publication No. 2002-069660

Summary of Invention

Technical Problem

45 **[0009]** An aspect of the present disclosure is to improve pitting corrosion resistance and blackening resistance of a steel sheet by controlling a composition of a coating solution applied to a surface of a highly corrosion-resistant plated steel sheet and provide a solution composition having excellent solution stability and a steel sheet surface-treated using the solution composition, and a manufacturing method therefor.

50 **[0010]** The object of the present disclosure is not limited to the aforementioned content. The object of the present disclosure may be understood from the overall content of the present specification, and those skilled in the art will have no difficulty in understanding an additional object of the present disclosure.

Solution to Problem

[0011] According to an aspect of the present disclosure, a solution composition for a surface treatment of a steel sheet

includes: (a) 20 to 60 wt% of a trivalent chromium compound, (b) 0.1 to 10 wt% of an acidity regulator, (c) 1 to 20 wt% of an adhesion improver, (d) 1 to 20 wt% of a corrosion resistance improver, (e) 0.01 to 3.0 wt% of a pitting corrosion improver, (f) 1 to 20 wt% of a co-solvent, and (g) residual solvent.

[0012] According to another aspect of the present disclosure, a surface-treated plated steel sheet includes: a steel sheet; a Zn-Mg-Al-based plating layer formed on at least one surface of the steel sheet; and a surface treated coating layer formed on the plating layer, wherein the surface treated coating layer is a coating layer formed from the solution composition described above.

[0013] According to another aspect of the present disclosure, a method of manufacturing a surface-treated plated steel sheet includes: hot-dip galvanizing at least one surface of a steel sheet to form a Zn-Mg-Al-based plating layer; coating the plating layer with the solution composition described above; and drying the coated steel sheet.

Advantageous Effects of Invention

[0014] According to the present disclosure, a solution composition which is free from precipitation or agglomeration even when used after long-term storage and has excellent solution stability may be provided, and the steel sheet having excellent pitting corrosion resistance and blackening resistance may be provided by coating a steel sheet with the solution composition.

[0015] Furthermore, the lifespan of products may be improved by improving foreign matter defects during a coating process.

Brief Description of Drawings

[0016] FIG. 1 illustrates a plated steel sheet (a) in which pitting corrosion (edge portion) occurred and a plated steel sheet (b) in which surface corrosion did not occur, in an exemplary embodiment of the present disclosure.

Best Mode for Invention

[0017] The inventors of the present disclosure conducted in-depth research to obtain a solution composition advantageous in improving not only pitting corrosion resistance but also blackening resistance of a coated steel sheet when a steel sheet, such as a highly corrosion-resistant hot-dip galvanized steel material, is coated.

[0018] As a result, a solution composition in which a trivalent chromium compound is mixed with an acidity regulator, an adhesion improver, a corrosion resistance improver, a pitting corrosion improver, and a co-solvent in an appropriate amount may be provided, and this solution composition has high solution stability. Also, it was ascertained that an intended effect could be obtained when a steel sheet is surface-treated with the solution composition, thereby completing the present disclosure.

[0019] Hereinafter, the present disclosure is described in detail.

[0020] First, the solution composition for surface treatment of steel sheets according to an aspect of the present disclosure is described in detail.

[0021] The solution composition according to the present disclosure may include (a) 20 to 60 wt% of a trivalent chromium compound, (b) 0.1 to 10 wt% of an acidity regulator, (c) 1 to 20 wt% of an adhesion improver, (d) 1 to 20 wt% of a corrosion resistance improver, (e) 0.01 to 3.0 wt% of a pitting corrosion improver, (f) 1 to 20 wt% of a co-solvent, and (g) residual solvent.

[0022] The content of the solution composition of the present disclosure is based on 100 wt% of the total.

[0023] As to be described in detail below, the solution composition may form a coating layer on at least one surface of a substrate on which the composition may be applied. In the present disclosure, the substrate may be the aforementioned steel sheet, for example, a highly corrosion-resistant hot-dip galvanized steel sheet, and may be a Zn-Mg-Al-based alloy plated steel sheet, as a non-limiting example.

[0024] Hereinafter, each component constituting the solution composition is described in detail.

(a) 20 to 60 wt% of a trivalent chromium compound

[0025] In the solution composition of the present disclosure, the trivalent chromium compound mainly forms an insoluble film on a surface of the steel sheet, thereby improving corrosion resistance through a barrier effect.

[0026] If the content of the trivalent chromium compound in the solution composition of the present disclosure is less than 20%, a strong insoluble film can be insufficiently formed and moisture penetrating into the surface of the steel sheet cannot be effectively blocked, and as a result, corrosion resistance cannot be secured. In contrast, if the content exceeds 60%, there is a risk of foreign matter defects occurring due to an excessive chromium content.

[0027] In the present disclosure, the type of the trivalent chromium compound is not particularly limited but may be

one or more selected from the group consisting of chromium sulfate, chromium nitrate, chromium phosphate, chromium fluoride, chromium chloride, and mixtures thereof.

(b) 0.1 to 10 wt% of an acidity regulator

[0028] In the solution composition of the present disclosure, the acidity regulator controls the pH of the solution to ensure that the components in the composition exist stably in the solution and react appropriately under coating conditions to stably form a film.

[0029] If the content of the acidity regulator is less than 0.1%, the pH of the solution may increase and solution stability may deteriorate. In contrast, if the content exceeds 10%, corrosion resistance, etc., may not be secured due to residual acid after drying.

[0030] In the present disclosure, the type of acidity regulator is not particularly limited but may be one or more selected from the group consisting of phosphoric acid, nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, NaH_2PO_4 , Na_2HPO_4 , phytic acid, glycolic acid, lactic acid, acetic acid, oxalic acid, and mixtures thereof.

(c) 1 to 20 wt% of an adhesion improver

[0031] In the solution composition of the present disclosure, the adhesion improver combines with the trivalent chromium compound, and also with the steel sheet to improve the adhesion and corrosion resistance of the coating layer.

[0032] If the content of the adhesion improver is less than 1%, adhesion to the steel sheet may not be sufficiently secured and foreign matter defects may occur. In contrast, if the content exceeds 20%, the amount remaining after forming the coating film may be excessive, and corrosion resistance, etc., may not be secured.

[0033] There is no particular limitation to the type of the adhesion improver in the present disclosure, but may be one or more selected from the group consisting of vinyl methoxy silane, vinyl trimethoxy silane (VTMS), vinyl epoxy silane, vinyl triepoxy silane, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxy silane, 3-metaglyoxypropyltrimethoxy silane, γ -glycidoxypropyltriethoxysilane, γ -glycidoxytrimethyldimethoxysilane, N-(3-(trimethoxysilyl)propyl)ethylenediamine (AEAPTMS), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 3-(2,3-epoxypropoxy)propyltrimethoxysilane, 3-(2,3-epoxypropoxy)propyltriethoxysilane, 3-(2,3-epoxypropoxy)propylmethyldiethoxysilane, 3-(2,3-epoxypropoxy)propylmethyldimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl-3-aminopropyl)methyldimethoxysilane, N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, diethylenetriaminopropyltrimethoxysilane, 3-ureidopropyltrimethoxysilane, N-phenylaminopropyltrimethoxysilane, (3-glycidyloxypropyl)trimethoxysilane (GPTMS), methyltrimethoxysilane (MTMS), and mixtures thereof.

(d) 1 to 20 wt% of a corrosion resistance improver

[0034] In the solution composition of the present disclosure, the corrosion resistance improver serves to fill a gap that may exist between the trivalent chromium compound and the adhesion improver, etc. and form a passive film to suppress corrosion.

[0035] If the content of the corrosion resistance improver is less than 1%, a passive film can be insufficiently formed, and thus, it may be difficult to secure corrosion resistance, whereas if the content exceeds 20%, solution stability may be reduced due to excessively high solid content.

[0036] In the present disclosure, the type of the corrosion resistance improver is not particularly limited, but may be one or more selected from the group consisting of vanadyl acetylacetonate, ammonium metavanadate, potassium metavanadate, sodium metavanadate, vanadium trioxide, vanadium acetylacetate, ammonium metavanadate, silicon oxide, and mixtures thereof.

(e) 0.01 to 3.0 wt% of a pitting corrosion improver

[0037] In the solution composition of the present disclosure, the pitting corrosion improver acts, together with the corrosion resistance improver, to prevent local penetration of corrosion factors to thereby minimize pitting corrosion that occurs in the form of pitting.

[0038] If the content of the pitting corrosion improver in the solution composition of the present disclosure is less than 0.01 %, there is a problem in that pitting corrosion may occur because local penetration of corrosion factors may not be blocked. Meanwhile, if the content exceeds 3.0 %, pH of the solution may increase excessively and solution stability may decrease.

[0039] In the present disclosure, the type of the pitting corrosion improver is not particularly limited but may be, preferably, one or more selected from the group consisting of ethylenediamine, hexamethylenediamine, trimethylamine,

methyllamine, diphenylamine, ethyleneamine, aniline, toluidine, piperidine, aziridine, pyridine, alanine, propylamine, diisopropylamine, monoisopropylamine, dibutylamine, dipropylamine, and mixtures thereof.

(f) 1 to 20 wt% of a co-solvent

[0040] In the solution composition of the present disclosure, the co-solvent serves to control a volatilization rate of the solvent during a drying process of the coating operation to suppress defects on the film surface after drying.

[0041] If the content of the co-solvent is less than 1%, the effect of controlling the volatilization rate during drying may be insufficient and an evaporation rate of a main solvent may rapidly boil at a boiling point, causing surface defects of so-called popping, which leads to a decrease in corrosion resistance, etc. In contrast, if the content exceeds 20%, solution stability may decrease due to rapid changes in the viscosity and density of the solution.

[0042] In the present disclosure, the type of co-solvent is not particularly limited, but may be one or more selected from the group consisting of ethanol, isopropyl alcohol, methanol, tallow alcohol, 2-butoxyethanol, diethylene glycol monobutyl ether, and mixtures thereof.

(g) Solvent

[0043] The solution composition of the present disclosure may include a solvent as a residual component, and water (distilled water, deionized water) may be used as the solvent in the present disclosure.

[0044] Hereinafter, a steel sheet surface-treated with the aforementioned solution composition according to another aspect of the present disclosure to include a certain coating layer is described in detail.

[0045] In the present disclosure, the composition may be surface-treated on a plated steel sheet, and preferably on a ternary (Zn-Mg-Al-based) hot-dip galvanized steel sheet.

[0046] That is, the surface-treated steel sheet of the present disclosure may include a steel sheet; a Zn-Mg-Al-based plating layer formed on at least one surface of the steel sheet; and a surface-treated coating layer formed on the plating layer.

[0047] Here, the steel sheet is a base steel sheet from which a plated steel sheet may be obtained, and in particular, the steel sheet may be any steel sheet from which a ternary (Zn-Mg-Al-based) hot-dip galvanized steel sheet may be obtained.

[0048] The composition of the Zn-Mg-Al-based plating layer may include, in wt%, magnesium (Mg): 4.0 to 7.0 %, aluminum (Al): 11.0 to 19.5 %, a balance of Zn, and other inevitable impurities.

[0049] Magnesium (Mg) in the plating layer is an element that plays a role in improving the corrosion resistance of the plated steel sheet, and the content of magnesium (Mg) is preferably 4.0% or more to ensure the excellent corrosion resistance intended in the present disclosure. However, if the content of Mg is excessive, there is a risk of dross that may occur in a plating bath and there is a risk of excessively forming high hardness intermetallic compounds in the plating layer to deteriorate the bendability of the steel sheet, and thus, the content of magnesium may be limited to 7.0%.

[0050] Meanwhile, when the Mg content is added by 4.0% or more, there is a risk of the occurrence of dross due to Mg oxidation in the plating bath, so considering this, it is preferable to include aluminum (Al) by 11.0% or more. However, if the Al content is excessive, a melting point of the plating bath may increase and an operating temperature accordingly may become excessively high, which may cause problems due to high-temperature work, such as erosion of the plating bath structure and deterioration of the steel sheet. Therefore, the Al content may be limited to 19.5% or less.

[0051] The residual composition, excluding Mg and Al, is zinc (Zn), and inevitable impurities may be unintentionally mixed in the process of manufacturing a plated steel sheet with a Zn-Mg-Al-based plating layer. At this time, it should be noted that those skilled in the art may easily understand the meaning of inevitable impurities.

[0052] It is preferable that the structure of the aforementioned Zn-Mg-Al-based plating layer satisfies the following [Relational Expression 1].

[Relational Expression 1]

$$0.26 \leq I(110)/I(103) \leq 0.65$$

[0053] (In Relational Expression 1, I(110) represents an X-ray diffraction integrated intensity of the (110) plane crystal peak for the MgZn₂ phase, and I(103) represents the represents an X-ray diffraction integrated intensity of the (103) plane crystal for the MgZn₂ phase.)

[0054] In the present disclosure, the bendability, whiteness, etc. of the plated steel sheet may be secured by controlling the MgZn₂ phase of the Zn-Mg-Al-based plating layer using the above [Relational Expression 1].

[0055] If the value defined by the [Relational Expression 1] is less than 0.26, the ratio of the presence of (103) plane

crystal for the MgZn_2 phase to the (110) plane crystal for the MgZn_2 phase may be excessive and bendability or whiteness may become insufficient. Meanwhile, if the above value exceeds 0.65, the ratio of the presence of (110) plane crystal for the MgZn_2 phase to the (103) plane crystal for the MgZn_2 phase may be too excessive and an increase in diffuse reflection cannot be induced, leading to insufficient whiteness.

[0056] At this time, the $I(110)$ may have an integrated intensity value in the range of 120 to 200, and the $I(103)$ may have an integrated intensity value in the range of 240 to 300. In this manner, it is desirable to satisfy the value of [Relational Expression 1] within each range.

[0057] A coating layer formed by coating the composition of the present disclosure in a solution state may be provided on top of the aforementioned Zn-Mg-Al-based plating layer, and in this case, the coating layer preferably has a thickness of 0.1 to 2.0 μm .

[0058] If the thickness of the coating layer is less than 0.1 μm , there is a problem that the surface treatment solution composition is applied thinly to a crest portion of roughness existing on the surface of the plated steel sheet, resulting in a decrease in corrosion resistance. Meanwhile, if the thickness exceeds 2.0 μm , the coating layer may be formed thickly, which may deteriorate processability and increase the cost of solution treatment, making it economically disadvantageous.

[0059] Here, the thickness refers to a thickness after drying.

[0060] In addition, a method of manufacturing a surface-treated steel sheet using the composition of the present disclosure is described.

[0061] In detail, the method may include: hot-dip galvanizing at least one surface of a steel sheet to form a Zn-Mg-Al-based plating layer; applying the composition of the present disclosure in a solution state to the plating layer to coat the steel sheet; and drying the coated steel sheet.

[0062] When applying the composition of the present disclosure to the steel sheet in a solution state, a commonly used coating method may be applied, so there is no particular limitation.

[0063] For example, the coating process may be performed by selecting one method among methods, such as bar coating, roll coating, spraying, dipping, spray squeezing, and immersion squeezing.

[0064] The process of drying the steel sheet coated with the composition is preferably carried out in a temperature range of 40 to 280°C based on a peak metal temperature (PMT) of a steel sheet.

[0065] If the temperature of the steel sheet is less than 40°C based on the PMT, the formation of a strong film structure may be insufficient, and there is a risk that corrosion resistance and blackening resistance may be deteriorated. Meanwhile, if the temperature exceeds 280°C, hardness of the film may increase excessively, resulting in poor corrosion resistance of processed parts, and poor surface quality, such as yellowing due to excessive heat.

[0066] The steel sheet on which the drying treatment has been completed may have a coating layer with a thickness of 0.1 to 2.0 μm after drying.

[0067] In the present disclosure, the unit for performing the drying treatment are not particularly limited, but it is noted that equipment, such as an induction oven or hot air drying furnace, may be used, and the conditions of these equipment may be conventional conditions.

[0068] Hereinafter, the present disclosure is described in more detail through examples. However, the description of these examples is only for illustrating the implementation of the present disclosure, and the present disclosure is not limited by the description of these examples. This is because the scope of the present disclosure is determined by matters stated in the claims and matters reasonably inferred therefrom.

[Mode for invention]

[Preparation of solution composition for surface treatment of steel sheet]

[0069] In order to measure the physical properties of the solution composition for surface treatment of a steel sheet of the present disclosure, the solution composition was prepared using the following materials.

[0070] First, after phosphoric acid was added as an acidity regulator to distilled water (solvent), chromium nitrate, a trivalent chromium compound, was added at about 40°C and then stirred for about 30 minutes. In the same manner, (3-glycidyloxypropyl)trimethoxysilane (GPTMS), as an adhesion improver, silicon oxide as a corrosion resistance improver, ethylenediamine as a pitting corrosion improver, and ethanol as a co-solvent were added and stirred at 30-minute intervals.

[0071] Here, the content of each component is shown in Table 1 below.

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[Table 1]

5	Classification	Trivalent chromium compound	Acidity regulator	Adhesion improver	Corrosion resistance improver	Pitting corrosion improver	Co-solvent	Solvent
	Inventive Example 1	55	0.5	3	5	0.5	3	33
10	Inventive Example 2	23	4	12	9	3	3	46
	Inventive Example 3	43	8	5	8	2	9	25
15	Inventive Example 4	49	0.3	6	9	1	5	29.7
	Inventive Example 5	25	4	2	10	1	20	38
20	Inventive Example 6	22	6	18	12	1	15	26
	Inventive Example 7	40	9	3	18	1	8	21
25	Inventive Example 8	50	2	18	2	3	7	18
	Inventive Example 9	23	2	11	8	0.1	1	54.9
30	Inventive Example 10	56	3	1	2	2.8	5	30.2
	Inventive Example 11	28	10	7	11	1	2	41
35	Inventive Example 12	33	1	4	6	1	18	37
	Comparative Example 1	<u>15</u>	8	3	17	1	10	46
40	Comparative Example 2	<u>65</u>	1	10	2	1	2	19
	Comparative Example 3	49	<u>0</u>	15	8	1	5	22
45	Comparative Example 4	57	<u>11</u>	2	1	1	9	19
	Comparative Example 5	38	3	<u>0.1</u>	12	2	5	39.9
50	Comparative Example 6	41	3	<u>22</u>	7	3	6	18
	Comparative Example 7	32	4	18	<u>0.2</u>	1	3	41.8
55	Comparative Example 8	26	9	6	<u>23</u>	3	4	29
	Comparative Example 9	34	6	12	20	<u>0</u>	6	22

(continued)

Classification	Trivalent chromium compound	Acidity regulator	Adhesion improver	Corrosion resistance improver	Pitting corrosion improver	Co-solvent	Solvent
Comparative Example 10	45	5	16	16	<u>4</u>	8	6
Comparative Example 11	47	2	13	6	1	<u>0</u>	31
Comparative Example 12	32	3	7	6	1	<u>30</u>	21

Solution stability

[0072] The following experiment was conducted to confirm that the prepared solution composition maintained solution stability under certain conditions.

[0073] The initial viscosity V_i of each solution composition of Invention Examples 1 to 12 and Comparative Examples 1 to 12 was measured, and then each solution composition was stored in an oven at 50°C for 120 hours, cooled to 25°C, and the viscosity V_f at 25°C was then measured. Each measured viscosity value was substituted into Equation 1 below, and solution stability was evaluated according to the calculated value ΔV . The results are shown in Table 3 below.

[Equation 1]

$$\Delta V = (V_f - V_i) / V_i \times 100 (\%)$$

<Criteria for evaluating solution stability>

[0074]

○: Value ΔV is less than 20 %, or a gelation phenomenon is not visible when observed with the naked eye.

×: Value ΔV is 20 % or more, or the gelation phenomenon is visible when observed with the naked eye

[Manufacture of surface-treated steel sheet]

[0075] Next, the prepared solution composition was applied to the surface of the steel sheet using a bar coating method and dried in an induction oven to obtain each surface-treated steel sheet. The bar coating was carried out so that the adhesion amount of the composition was about 35 mg/m² based on Cr.

[0076] Here, as the steel sheet for applying the solution composition, a Zn-Mg-Al-based alloy hot-dip galvanized steel sheet (plating layer: 5.4 w% of Mg, 12.6 w% of Al, balance Zn and inevitable impurities, value of [Relational Expression 1]: 0.40) was used, and it was cut into 7 cm × 15 cm (width × height) and produced as a degreased specimen.

[0077] The drying temperature during the surface treatment and thickness of the formed coating layer are shown in Table 2 below.

[Table 2]

Classification	Heat-treatment temperature (°C)	Thickness of coating layer (μm)
Inventive Example 1	60	0.5
Inventive Example 2	60	0.5
Inventive Example 3	60	0.5
Inventive Example 4	60	0.5
Inventive Example 5	60	0.5
Inventive Example 6	60	0.5

(continued)

Classification	Heat-treatment temperature (°C)	Thickness of coating layer (μm)
Inventive Example 7	60	0.5
Inventive Example 8	160	0.5
Inventive Example 9	160	0.5
Inventive Example 10	160	1.1
Inventive Example 11	220	1.1
Inventive Example 12	220	1.1
Comparative Example 1	60	1.1
Comparative Example 2	60	1.1
Comparative Example 3	60	1.1
Comparative Example 4	60	1.1
Comparative Example 5	60	1.1
Comparative Example 6	160	1.1
Comparative Example 7	160	1.1
Comparative Example 8	160	1.1
Comparative Example 9	220	1.1
Comparative Example 10	220	1.1
Comparative Example 11	220	0.5
Comparative Example 12	220	0.5

[0078] In order to measure the physical properties of the surface-treated steel sheet manufactured as described above, plate corrosion resistance, processing part corrosion resistance, pipe forming oil infiltration, alkali resistance, pitting corrosion resistance, foreign matter defects, etc. were measured using the following methods and standards. Each result is shown in Table 3 below.

Plate corrosion resistance

[0079] Based on the method specified in ASTM B117, each steel sheet (specimen) was treated with the solution composition and a white rust incidence rate of the steel sheet was measured over time.

<Criteria for evaluating plate corrosion resistance >

[0080]

- : White rust occurrence time is 144 hours or more.
- △: White rust occurrence time is 96 or more hours and less than 144 hours.
- ×: White rust occurrence time is less than 96 hours

Corrosion resistance of processed parts

[0081] The steel sheet (specimen) surface-treated as described above was pushed up to a height of 6 mm using an Erichsen tester, and the occurrence degree of white rust was measured after 24 hours.

<Criteria for evaluating corrosion resistance of processed parts>

[0082]

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◦: White rust does not occur, or white rust is very subtle, if present

△: White rust occurs in a circle and partially flows but does not flow out of the circle

×: White rust occurs and flows out of the circle

5 Pipe forming oil infiltration

[0083] The steel sheet (specimen) surface-treated as described above was immersed in forming oil at room temperature, maintained for 24 hours, and a color difference before and after immersion was measured. At this time, the forming oil used was domestic BW WELL MP-411 diluted in 10% water.

10

<Criteria for evaluating pipe forming oil infiltration>

[0084]

15

◦:

$$\Delta E \leq 2$$

20

△:

$$2 < \Delta E \leq 3$$

25

×:

$$3 < \Delta E$$

30 Alkali resistance

[0085] The steel sheet (specimen) surface-treated as described above was immersed in a degreasing solution at 60°C for 2 minutes, then washed with water and air-blown, and a color difference before and after was measured. At this time, the alkaline degreasing solution used was Parkerizing's Finecleaner L 4460 A: 20g/2.4L + L 4460 B: 12g/2.4L (pH=12).

35

<Criteria for evaluating alkali resistance>

[0086]

40

◦:

$$\Delta E \leq 2$$

45

△:

$$2 < \Delta E \leq 4$$

50

×:

$$4 < \Delta E$$

55 Pitting corrosion resistance

[0087] Dew was formed on the surface of the steel sheet (specimen) surface-treated as described above using a sprayer, then two sprayed steel sheets were placed into contact with each other, packed, placed in a constant temperature

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and humidity chamber, and conducted for total 8 cycles in which 6 hours at high temperature and humidity (42°C, 95%) and 6 hours at low temperature and humidity (15°C, 60%) were set to one cycle, and thereafter, the number of pitting defects on the surface was measured. At this time, a scan area of the steel sheet was set to 150×50mm², which was enlarged to 100 times, and only the number of corrosive pitting defect area of 29500 μm² or more was counted.

<Criteria for evaluating pitting corrosion resistance>

[0088]

○:

Number of pitting ≤ 20

△:

20 < number of pitting ≤ 40

×:

40 < number of pitting

Foreign matter defect

[0089] In order to evaluate foreign matter defects in the steel sheet (specimen) surface-treated as described above, a probe having a surface area of about 4 cm² was covered with white gauze, a weight of 10 kg was placed on the probe, the probe was brought into friction-contact in a reciprocating manner on the surface of the steel sheet 100 times, and then, a whiteness value ($\Delta L = L_{\text{before}} - L_{\text{after}}$) of the gauze before and after frictional contact was measured. At this time, in order to simulate high humidity conditions, the steel sheet and the probe were placed in a humidity chamber, 95% or more humidity was maintained in the chamber using a humidifier, and then evaluation of frictional contact was conducted.

<Criteria for evaluating foreign matter defect>

[0090]

○:

$\Delta L \leq 2.5$

△:

2.5 < $\Delta L \leq 5.0$

×:

5.0 < ΔL

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[Table 3]

5	Classification	Solution stability	Plate corrosion resistance	Corrosion resistance of processed parts	Pipe forming oil infiltration	Alkali resistance	Pitting corrosion resistance	Foreign matter defects
	Inventive Example 1	○	○	○	○	○	○	○
10	Inventive Example 2	○	○	○	○	○	○	○
	Inventive Example 3	○	○	○	○	○	○	○
15	Inventive Example 4	○	○	○	○	○	○	○
	Inventive Example 5	○	○	○	○	○	○	○
20	Inventive Example 6	○	○	○	○	○	○	○
	Inventive Example 7	○	○	○	○	○	○	○
25	Inventive Example 8	○	○	○	○	○	○	○
	Inventive Example 9	○	○	○	○	○	○	○
30	Inventive Example 10	○	○	○	○	○	○	○
	Inventive Example 11	○	○	○	○	○	○	○
35	Inventive Example 12	○	○	○	○	○	○	○
	Comparative Example 1	○	×	×	○	○	×	○
40	Comparative Example 2	○	○	○	○	○	○	×
	Comparative Example 3	×	×	×	○	○	×	○
45	Comparative Example 4	○	×	×	○	○	×	○
	Comparative Example 5	○	○	○	○	○	○	×
50	Comparative Example 6	○	×	×	○	○	×	○
	Comparative Example 7	○	×	×	○	○	×	○
55	Comparative Example 8	×	○	○	○	×	○	×
	Comparative Example 9	○	○	○	○	○	×	○

(continued)

Classificat ion	Solutio n stabili ty	Plate corrosi on resista nce	Corrosi on resista nce of process ed parts	Pipe forming oil infiltrat ion	Alkali resista nce	Pitting corrosi on resista nce	Forei gn matte r defec ts
Comparative Example 10	×	○	×	○	○	○	○
Comparative Example 11	○	×	×	○	○	×	○
Comparative Example 12	×	○	×	○	○	○	○

[0091] As shown in Table 3, the solution compositions of Inventive Examples 1 to 12 had excellent solution stability, and steel sheets surface-treated with the solution composition also showed excellent results in all evaluation results.

[0092] Meanwhile, Comparative Example 1 was a case in which the content of the trivalent chromium compound was insufficient, and the corrosion resistance due to the barrier effect was not sufficient, resulting in poor plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance.

[0093] In Comparative Example 2, the content of the trivalent chromium compound was excessively high, and it can be seen that foreign matter defects occurred.

[0094] In Comparative Example 3, the solution stability was inferior due to an insufficient amount of acidity regulator, and the plate corrosion resistance, the corrosion resistance of processed parts, and the pitting corrosion resistance of the steel sheet surface-treated with the solution composition were inferior.

[0095] Comparative Example 4 was a case in which the content of the acidity regulator was excessive, and the amount of acid remaining in the solution increased, resulting in poor plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance of the surface-treated steel sheet.

[0096] Comparative Example 5 was a case in which the content of the adhesion improver was insufficient, and foreign matter defects occurred.

[0097] Comparative Example 6 was a case in which the content of the adhesion improver was excessively high, and the surface-treated steel sheet was inferior in plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance due to remaining unreacted silane.

[0098] Comparative Example 7 was a case in which the content of the corrosion resistance improver was insufficient, and the corrosion resistance was not sufficient, resulting in poor plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance.

[0099] In Comparative Example 8, the content of the corrosion resistance improver was excessive, and the solution stability was inferior due to the excessively increased solid content, the alkali resistance of the surface-treated steel sheet was inferior, and foreign matter defects occurred.

[0100] Comparative Example 9 was a case in which the content of the pitting corrosion improver was insufficient, and the pitting corrosion resistance of the surface-treated steel sheet was poor.

[0101] Comparative Example 10 was a case in which the content of the pitting corrosion improver was excessive, resulting in insufficient solution stability and corrosion resistance of processed parts of the surface-treated steel sheet.

[0102] Comparative Example 11 was a case in which the content of the co-solvent was insufficient, and the surface-treated steel sheet had inferior plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance.

[0103] Comparative Example 12 was a case in which the content of the co-solvent was excessive, the solution stability was insufficient, and the corrosion resistance of processed parts of the surface-treated steel sheet was poor.

[0104] FIG. 1 illustrates a surface shape of the steel sheet (Inventive Example 1) surface-treated using the solution composition according to the present disclosure and a surface shape of the steel sheet surface-treated using the related art composition.

[0105] As shown in FIG. 1, it can be seen that, the steel sheet (a) surface-treated with the related art solution composition had the pitting corrosion defects at the edge portion, whereas the steel sheet (b) surface-treated with the solution composition of the present disclosure had a smooth surface up to the edge portion without defects.

Claims

1. A solution composition for a surface treatment of a steel sheet, the solution composition comprising:

- (a) 20 to 60 wt% of trivalent chromium compound,
- (b) 0.1 to 10 wt% of acidity regulator,
- (c) 1 to 20 wt% of adhesion improver,
- (d) 1 to 20 wt% of corrosion resistance improver,
- (e) 0.01 to 3.0 wt% of pitting corrosion improver,
- (f) 1 to 20 wt% of co-solvent, and
- (g) a residual solvent

2. The solution composition of claim 1, wherein the trivalent chromium compound is one or more selected from the group consisting of chromium sulfate, chromium nitrate, chromium phosphate, chromium fluoride, chromium chloride, and mixtures thereof.

3. The solution composition of claim 1, wherein the acidity regulator is one or more selected from the group consisting of phosphoric acid, nitric acid, sulfuric acid, hydrofluoric acid, hydrochloric acid, $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, NaH_2PO_4 , Na_2HPO_4 , phytic acid, glycolic acid, lactic acid, acetic acid, oxalic acid, and mixtures thereof.

4. The solution composition of claim 1, wherein the adhesion improver is one or more selected from the group consisting of vinyl methoxy silane, vinyl trimethoxy silane (VTMS), vinyl epoxy silane, vinyl triepoxy silane, 3-aminopropyltriethoxy silane, 3-glycidoxypolytrimethoxy silane, 3-metaglyoxypolytrimethoxy silane, γ -glycidoxypolytriethoxysilane, γ -glycidoxypolytrimethoxydimethoxysilane, N-(3-(trimethoxysilyl)propyl)ethylenediamine (AEAPTMS), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, 3-(2,3-epoxypropoxy)propyltrimethoxysilane, 3-(2,3-epoxypropoxy)propyltriethoxysilane, 3-(2,3-epoxypropoxy)propylmethyldiethoxysilane, 3-(2,3-epoxypropoxy)propylmethyldimethoxysilane, 3-aminopropyltriethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropylmethyldiethoxysilane, N-(2-aminoethyl-3-aminopropyl)methyldimethoxysilane, N-(2-aminoethyl-3-aminopropyl)trimethoxysilane, diethylenetriaminopropyltrimethoxysilane, 3-ureidopropyltrimethoxysilane, N-phenylaminopropyltrimethoxysilane, (3-glycidylpropoxy)trimethoxysilane (GPTMS), methyltrimethoxysilane (MTMS), and mixtures thereof.

5. The solution composition of claim 1, wherein the corrosion resistance improver is one or more selected from the group consisting of vanadyl acetylacetonate, ammonium metavanadate, potassium metavanadate, sodium metavanadate, vanadium trioxide, vanadium acetylacetate, ammonium metavanadate, silicon oxide, and mixtures thereof.

6. The solution composition of claim 1, wherein the pitting corrosion improver is one or more selected from the group consisting of ethylenediamine, hexamethylenediamine, trimethylamine, methylamine, diphenylamine, ethyleneamine, aniline, toluidine, piperidine, aziridine, pyridine, alanine, propylamine, diisopropylamine, monoisopropylamine, dibutylamine, dipropylamine, and mixtures thereof.

7. The solution composition of claim 1, wherein the co-solvent is one or more selected from the group consisting of ethanol, isopropyl alcohol, methanol, tallow alcohol, 2-butoxyethanol, diethylene glycol monobutyl ether, and mixtures thereof.

8. The solution composition of claim 1, wherein the solvent is water.

9. A surface-treated plated steel sheet comprising:

- a steel sheet;
 - a Zn-Mg-Al-based plating layer formed on at least one surface of the steel sheet; and
 - a surface treated coating layer formed on the plating layer,
- wherein the surface treated coating layer is a coating layer formed from the composition of any one of claims 1 to 8.

10. The surface-treated plated steel sheet of claim 9, wherein

the Zn-Mg-Al-based plating layer includes, in wt%, magnesium (Mg): 4.0 to 7.0 %, aluminum (Al): 11.0 to 19.5 %, a balance of Zn, and other inevitable impurities, and satisfies the following Relational Expression 1:

[Relational Expression 1]

$$0.26 \leq I(110)/I(103) \leq 0.65$$

5

(In Relational Expression 1, I(110) represents an X-ray diffraction integrated intensity of the (110) plane crystal peak for the MgZn₂ phase, and I(103) represents the represents an X-ray diffraction integrated intensity of the (103) plane crystal for the MgZn₂ phase.)

10 **11.** The surface-treated plated steel sheet of claim 9, wherein the surface treated coating layer has a thickness of 0.1 to 2.0 μm.

12. A method of manufacturing a surface-treated plated steel sheet, the method comprising:

15 hot-dip galvanizing at least one surface of a steel sheet to form a Zn-Mg-Al-based plating layer;
coating the plating layer with the composition of any one of claims 1 to 8; and
drying the coated steel sheet.

20 **13.** The method of claim 12, wherein the coating is performed by one method selected from the group consisting of bar coating, roll coating, spraying, dipping, spray squeezing, and immersion squeezing.

14. The method of claim 12, wherein the drying is carried out in a temperature range of 40 to 280°C based on a peak metal temperature (PMT) of the steel sheet.

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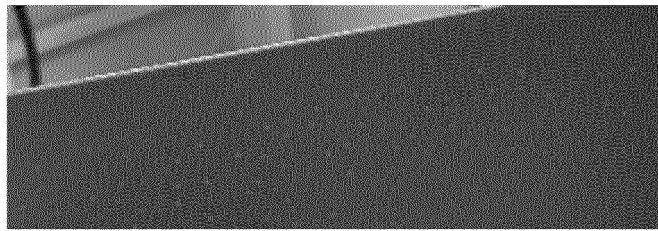
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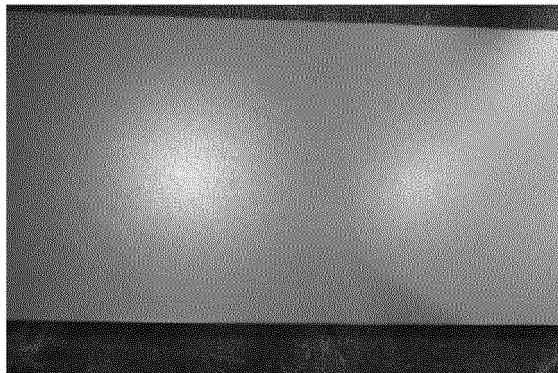
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55



(a)



(b)

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/020708

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/50(2006.01)i; C23C 22/06(2006.01)i; C23C 2/26(2006.01)i; C23C 2/06(2006.01)i; C23C 2/40(2006.01)i;
C23C 28/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 22/50(2006.01); B05D 7/14(2006.01); C09D 5/08(2006.01); C09D 5/10(2006.01); C23C 22/05(2006.01);
C23C 22/08(2006.01); C23C 22/30(2006.01); C23C 22/38(2006.01); C23C 22/42(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS (KIPO internal) & keywords: 표면처리(surface treatment), 3가 크롬(trivalent chromium), 산도 조절제(acidity
regulator), 밀착성(adhesion), 내식성(corrosion resistance), 부식 개선(corrosion improvement)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2018-0135514 A (POSCO et al.) 21 December 2018 (2018-12-21) See paragraphs [0026] and [0029] and claims 1-2, 4, 7 and 9-14.	1-14
A	KR 10-1786358 B1 (POSCO et al.) 18 October 2017 (2017-10-18) See claims 1-6.	1-14
A	EP 3712300 A1 (POSCO) 23 September 2020 (2020-09-23) See claims 1-4.	1-14
A	JP 2019-536899 A (POSCO) 19 December 2019 (2019-12-19) See claims 1-7.	1-14
A	KR 10-0180735 B1 (NIHON PARKERIZING CO., LTD. et al.) 18 February 1999 (1999-02-18) See claims 1-5.	1-14

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

23 March 2023

Date of mailing of the international search report

24 March 2023

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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