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

(57) The present invention relates to: a solution composition capable of improving corrosion-resistance and blackening-resistance of a steel sheet; a steel sheet sur-

face-treated using same; and a method for manufacturing the steel sheet.

(a)



(b)

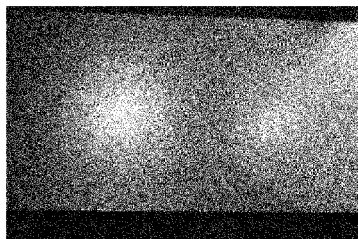


FIG. 1

Description

Technical Field

[0001] The present disclosure relates to a solution composition capable of improving 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

[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 of 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.

[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.

[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.

[Related Art Document]

[0008]

(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

[0009] An aspect of the present disclosure is to improve external 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.

[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) 0.1 to 10 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 15 wt% of corrosion resistance improver, (e) 0.1 to 25 wt% of film former, (f) 0.01 to 2 wt% of lubricant, (g) 0.5 to 10 wt% of co-solvent, and (h) a residual solvent.

[0012] According to another aspect of the present disclosure, a surface-treated steel sheet includes: a steel sheet; and a coating layer formed on at least one surface of the steel sheet, in which the coating layer is formed of the solution composition described above.

[0013] According to another aspect of the present disclosure, a method of manufacturing a surface-treated steel sheet includes: providing a steel sheet; applying the composition of any one of claims 1 to 9 on at least one surface of the steel sheet; and heat-treating the steel sheet coated with the composition at 50 to 250°C.

Advantageous Effects of Invention

[0014] According to the present disclosure, a solution composition having excellent solution stability may be provided, and a steel sheet having excellent 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 surface (edge portion) corrosion 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 corrosion resistance but also blackening resistance of a plated 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 film former, a lubricant, 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) 0.1 to 10 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 15 wt% of corrosion resistance improver, (e) 0.1 to 25 wt% of film former, (f) 0.01 to 2 wt% of lubricant, (g) 0.5 to 10 wt% of co-solvent, and (h) a 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) 0.1 to 10 wt% of 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 0.1%, 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 10%, 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 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 adhesion improver

[0031] In the solution composition of the present disclosure, the adhesion improver combines with the trivalent chromium compound and the film former, 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-glycidoxypolytrimethoxy silane, 3-metaxyloxypropyltrimethoxy 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-aminopropyltriethoxysilane, 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 15 wt% of 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 film former 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 15%, 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 acetylacetonate, ammonium metavanadate, silicon oxide, and mixtures thereof.

(e) 0.1 to 25 wt% of film former

[0037] In the solution composition of the present disclosure, the film former is an ingredient added to form a strong film layer on the surface of the steel sheet along with the trivalent chromium compound, the adhesion improver, and a crosslinking agent. In other words, the film former may be advantageous for improving alkali resistance and pipe forming oil infiltration of the steel sheet by improving the film forming effect, which is insufficient with inorganic ingredients alone.

[0038] If the content of the film former is less than 0.1%, film formation may be insufficient, making it difficult to secure the pipe forming oil infiltration and alkali resistance. In contrast, if the content exceeds 25%, there is a risk of the occurrence of foreign matter defects.

[0039] In the present disclosure, the type of the film former is not particularly limited, but may be one or more selected from the group consisting of polyurethane resin (cationic or non-ionic), acrylic emulsion (cationic or non-ionic), and mixtures thereof.

(f) 0.01 to 2 wt% of lubricant

[0040] In the solution composition of the present disclosure, the lubricant improves slip properties of the surface of the steel sheet, thereby improving processability and suppressing the occurrence of foreign material defects.

[0041] If the content of this lubricant is less than 0.01%, the slip properties of the surface of the steel sheet may be insufficient and there is a risk of the occurrence of foreign matter defects. In contrast, if the content exceeds 2%, solution stability may decrease.

[0042] In the present disclosure, the type of lubricant is not particularly limited, but may be one or more selected from the group consisting of polytetrafluoroethylene (PTFE), polyethylene (PE), carnauba-based wax, and mixtures thereof.

(g) 0.5 to 10 wt% of co-solvent

[0043] 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.

[0044] If the content of the co-solvent is less than 0.5%, 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 10%, solution stability may decrease due to rapid changes in the viscosity and density of the solution.

[0045] 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.

(h) Solvent

[0046] 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.

[0047] 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.

[0048] There is no particular limitation to the steel sheet that may be surface-treated with the solution composition in the present disclosure, but the steel sheet may be a plated steel sheet.

[0049] It is important to note that the plated steel sheet targeted in the present disclosure may be applied to all types of plated steel sheets, such as electroplated steel sheets, electroalloy galvanized steel sheets, alloyed hot-dip galvanized steel sheets, hot-dip aluminum-plated steel sheets, and aluminum-plated steel sheets.

[0050] However, as a non-limiting example, it should be noted that the plated steel sheet may be a hot-dip galvanized steel sheet or a ternary (Zn-Mg-Al-based) hot-dip galvanized steel sheet.

[0051] At least one surface of the aforementioned plated steel sheet may be coated with the solution composition of the present disclosure to form a coating layer on the surface of the plated steel sheet. Here, the coating layer may be formed to have a thickness of 0.2 to 3.0 μm on the plating layer of the plated steel sheet.

[0052] If the thickness of the coating layer is less than 0.2 μm , the effects of the coating layer, such as corrosion resistance, blackening resistance, and or the like, may not be sufficiently obtained. In contrast, if the thickness exceeds 3.0 μm , the coating layer may fall off due to frictional contact with a roll in contact therewith during a continuous operation for forming the coating layer, and as a result, there may be a risk of the occurrence of foreign matter defects.

[0053] Here, the thickness refers to a thickness after drying.

[0054] In addition, a method of manufacturing a surface-treated steel sheet using the solution composition of the present disclosure is described.

[0055] Specifically, the method of manufacturing a surface-treated steel sheet using the solution composition of the present disclosure may include providing a steel sheet; applying the solution composition of the present disclosure to at least one surface of the steel sheet; and heat-treating the steel sheet to which the composition is applied.

[0056] The steel sheet may be the aforementioned plated steel sheet and may be a hot-dip galvanized steel sheet or a ternary (Zn-Mg-Al-based) hot-dip galvanized steel sheet, as a non-limiting example.

[0057] When applying the solution composition of the present disclosure to the steel sheet, a commonly used coating method may be applied, so there is no particular limitation.

[0058] For example, one of methods, such as bar coating, roll coating, spray coating, and dipping coating, may be selectively applied.

[0059] Meanwhile, a coating layer may be formed to have a certain thickness by heat-treating the steel sheet to which the composition has been applied using the aforementioned coating method.

[0060] At this time, heat treatment is preferably performed in the temperature range of 50 to 250°C. If the heat treatment temperature is less than 50°C, a proper solid coating layer may not be formed and a liquid solution may remain, making

it impossible to secure target corrosion resistance. In contrast, if the temperature exceeds 250°C, there is a problem of deterioration and discoloration of the film layer due to the excessively high temperature, which may result in poor corrosion resistance and blackening resistance.

[0061] The present disclosure may also include a process of drying the composition applied during the heat treatment process so that the composition has a solid shape, and the steel sheet on which the heat treatment is completed may have a coating layer having a thickness of 0.2 to 3.0 μm after drying. Here, the drying method is not particularly limited, but it is noted that facilities, such as a hot air drying furnace or an induction heating furnace (induction oven) may be used, and drying conditions may be based on general methods.

[0062] 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]

[0063] 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.

[0064] 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-glycidioxypropyltrimethoxysilane as an adhesion improver, silicon oxide as a corrosion resistance improver, a urethane resin as a film former, PE wax as a lubricant, and ethanol as a co-solvent were added and stirred at 30-minute intervals.

[0065] Here, the content of each component is shown in Table 1 below.

[Table 1]

Classificat ion	Trivale nt chromiu m compoun d	Acidity regulat or	Adhesi on improv er	Corrosio n resistan ce improver	Film form er	Lubrica nt	Co-solve nt	Solve nt
Inventive Example 1	0.5	6.0	18.0	6.0	3.0	0.1	2.0	64.4
Inventive Example 2	2.0	6.0	10.0	2.0	6.0	1.8	0.8	71.4
Inventive Example 3	9.0	0.4	3.0	2.0	16.0	1.0	8.0	60.6
Inventive Example 4	4.0	3.0	8.0	14.0	3.0	1.0	3.0	64.0
Inventive Example 5	5.0	6.0	1.2	6.0	12.0	1.0	5.0	63.8
Inventive Example 6	4.0	7.0	4.0	5.0	11.0	1.0	7.0	61.0
Inventive Example 7	1.0	3.0	3.0	1.0	23.0	0.4	7.0	61.6
Inventive Example 8	2.0	9.0	6.0	2.0	11.0	1.0	8.0	61.0
Inventive Example 9	3.0	4.0	6.0	9.0	5.0	1.0	9.0	63.0
Inventive Example 10	2.0	2.0	11.0	2.0	10.0	2.0	10.0	61.0
Inventive Example 11	1.0	8.0	7.0	8.0	9.0	1.0	5.0	61.0

EP 4 455 362 A1

(continued)

5	Classificat ion	Trivale nt chromiu m compoun d	Acidity regulat or	Adhesi on improv er	Corrosio n resistan ce improver	Film form er	Lubrica nt	Co- solve nt	Solve nt
	Inventive Example 12	0.5	5.0	4.0	14.0	1.0	1.0	6.0	68.5
10	Inventive Example 13	2.0	8.0	13.0	6.0	2.0	1.0	6.0	62.0
	Inventive Example 14	2.0	0.5	19.0	3.0	6.0	2.0	4.0	63.5
15	Inventive Example 15	4.0	5.0	13.0	6.0	5.0	1.0	1.0	65.0
	Comparative Example 1	<u>0</u>	6.0	18.0	6.0	3.0	0.1	2.0	64.9
20	Comparative Example 2	<u>13.0</u>	6.0	3.0	2.0	6.0	1.0	8.0	61.0
	Comparative Example 3	2.0	<u>0</u>	10.0	2.0	6.0	1.8	0.8	77.4
25	Comparative Example 4	2.0	<u>14.0</u>	6.0	2.0	4.0	1.0	8.0	63.0
	Comparative Example 5	5.0	6.0	<u>0.1</u>	6.0	12.0	1.0	5.0	64.9
30	Comparative Example 6	2.0	0.5	<u>23.0</u>	3.0	4.0	2.0	4.0	61.5
	Comparative Example 7	1.0	3.0	3.0	<u>0.1</u>	13.0	0.4	7.0	72.5
35	Comparative Example 8	4.0	3.0	8.0	<u>17.0</u>	3.0	1.0	3.0	61.0
	Comparative Example 9	0.5	5.0	4.0	14.0	<u>0</u>	1.0	6.0	69.5
40	Comparative Example 10	2.0	2.0	1.5	2.0	<u>28.0</u>	1.0	5.0	58.5
	Comparative Example 11	3.0	4.0	6.0	9.0	5.0	<u>0</u>	9.0	64.0
45	Comparative Example 12	2.0	2.0	11.0	2.0	10.0	<u>2.5</u>	10.0	60.5
	Comparative Example 13	1.0	8.0	7.0	8.0	9.0	1.0	<u>0</u>	66.0
50	Comparative Example 14	2.0	8.0	6.0	6.0	2.0	1.0	<u>13.0</u>	62.0

Solution stability

55 **[0066]** The following experiment was conducted to confirm that the prepared solution composition maintained solution stability under certain conditions.

[0067] The initial viscosity V_i of each solution composition of Invention Examples 1 to 15 and Comparative Examples 1 to 14 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 VI at 25°C was then measured. Each measured viscosity value was substituted into Equation 1 below, and solution stability was evaluated according to the measured value ΔV . The results are shown in Table 3 below.

[Equation 1]

$$\Delta V = (VI - Vi) / Vi \times 100 (\%)$$

<Criteria for evaluating solution stability >

[0068]

○: 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]

[0069] Next, the prepared solution composition was applied to the surface of the steel sheet using a bar coating method and heat-treated by allowing the steel sheet to pass through an induction oven to obtain each surface-treated steel sheet. The bar coating was carried out so that a film adhesion amount was about 25 mg/m² based on Cr.

[0070] Here, a Zn-Al-Mg-based alloy hot-dip galvanized steel sheet (Al: 13.0%, Mg: 5.0%) was used as the steel sheet to which the solution composition is to be applied, and was cut into 7 cm × 15 cm (width × height) to produce a degreased specimen.

[0071] The heat treatment 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
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	160	1.1
Inventive Example 12	160	1.1
Inventive Example 13	160	1.1
Inventive Example 14	220	1.1
Inventive Example 15	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

(continued)

Classification	Heat-treatment temperature (°C)	Thickness of coating layer (μm)
Comparative Example 6	60	1.1
Comparative Example 7	60	1.1
Comparative Example 8	60	0.5
Comparative Example 9	60	0.5
Comparative Example 10	60	0.5
Comparative Example 11	60	0.5
Comparative Example 12	60	0.5
Comparative Example 13	60	0.5
Comparative Example 14	60	0.5

[0072] 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

[0073] 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 >

[0074]

- : 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

[0075] 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>

[0076]

- : White rust does not occur, or white rust is very subtle, if any
- △: 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

Pipe forming oil infiltration

[0077] 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.

<Criteria for evaluating pipe forming oil infiltration>

[0078]

EP 4 455 362 A1

○: $\Delta E \leq 2$

Δ : $2 < \Delta E \leq 3$

5 ×: $3 < \Delta E$

Alkali resistance

10 **[0079]** 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).

<Criteria for evaluating alkali resistance >

15 **[0080]**

○: $\Delta E \leq 2$

20 Δ : $2 < \Delta E \leq 4$

×: $4 < \Delta E$

Pitting corrosion resistance

25 **[0081]** 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 put into contact with each other, packed, placed in a constant temperature and humidity chamber, and conducted for 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
30 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>

35 **[0082]**

○: Number of pitting ≤ 20

Δ : $20 < \text{number of pitting} \leq 40$

40 ×: $40 < \text{number of pitting}$

Foreign matter defect

45 **[0083]** 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.
50

<Criteria for evaluating foreign matter defect >

[0084]

55 ○: $\Delta L \leq 2.5$

Δ : $2.5 < \Delta L \leq 5.0$

×: 5.0 < ΔL

[Table 3]

5	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
10	Inventive Example 1	○	○	○	○	○	○	○
	Inventive Example 2	○	○	○	○	○	○	○
15	Inventive Example 3	○	○	○	○	○	○	○
	Inventive Example 4	○	○	○	○	○	○	○
20	Inventive Example 5	○	○	○	○	○	○	○
	Inventive Example 6	○	○	○	○	○	○	○
25	Inventive Example 7	○	○	○	○	○	○	○
	Inventive Example 8	○	○	○	○	○	○	○
30	Inventive Example 9	○	○	○	○	○	○	○
	Inventive Example 10	○	○	○	○	○	○	○
35	Inventive Example 11	○	○	○	○	○	○	○
	Inventive Example 12	○	○	○	○	○	○	○
40	Inventive Example 13	○	○	○	○	○	○	○
	Inventive Example 14	○	○	○	○	○	○	○
45	Inventive Example 15	○	○	○	○	○	○	○
	Comparative Example 1	○	×	×	○	○	×	○
50	Comparative Example 2	○	○	○	○	○	○	×
	Comparative Example 3	×	×	×	○	○	○	○
55	Comparative Example 4	○	×	×	○	○	×	○
	Comparative Example 5	○	○	○	○	○	○	×

(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 6	○	×	×	○	○	×	○
Comparative Example 7	○	×	×	○	○	×	○
Comparative Example 8	×	○	○	○	×	○	×
Comparative Example 9	○	○	○	×	×	○	○
Comparative Example 10	○	○	○	○	○	○	×
Comparative Example 11	○	○	○	○	○	○	×
Comparative Example 12	×	○	×	○	○	○	○
Comparative Example 13	○	×	×	○	○	×	○
Comparative Example 14	×	○	×	○	○	○	○

[0085] As shown in Table 3, the solution compositions of Inventive Examples 1 to 15 had excellent solution stability, and steel sheets surface-treated with the solution composition also showed excellent results in all evaluation results.

[0086] Meanwhile, Comparative Example 1 was a case in which no trivalent chromium compound was added, 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.

[0087] In Comparative Example 2, the content of the trivalent chromium compound was excessively high, and it can be seen that foreign matter defects occurred.

[0088] In Comparative Example 3, in which no acidity regulator was added, the solution stability was inferior, and the plate corrosion resistance and the corrosion resistance of processed parts of the steel sheet surface-treated with the solution composition were inferior.

[0089] 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.

[0090] Comparative Example 5 was a case in which the content of the adhesion improver was insufficient, and foreign matter defects occurred.

[0091] 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.

[0092] 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.

[0093] 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.

[0094] Comparative Example 9 was a case in which no film former was added, and the surface-treated steel sheet had poor pipe forming oil infiltration and alkali resistance.

[0095] Comparative Example 10 was a case in which the content of the film former was excessive, and foreign matter defects occurred.

[0096] Comparative Example 11 was a case in which no lubricant was added, and foreign matter defects occurred.

[0097] Comparative Example 12 was a case in which the content of the lubricant was excessive, solution stability was insufficient, and the corrosion resistance of processed parts of the surface-treated steel sheet was poor.

[0098] Comparative Example 13 was a case in which no co-solvent was added, and not only did surface defects occur in the surface-treated steel sheet, but the corrosion resistance properties, such as plate corrosion resistance, corrosion resistance of processed parts, and pitting corrosion resistance were very poor.

[0099] Comparative Example 14 was a case in which the content of the co-solvent was excessive, and the solution stability was poor, and the corrosion resistance of processed parts of the surface-treated steel sheet was poor.

[0100] 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.

[0101] As shown in FIG. 1, it can be seen that, the steel sheet (a) surface-treated with the related art solution composition had 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) 0.1 to 10 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 15 wt% of corrosion resistance improver,
- (e) 0.1 to 25 wt% of film former,
- (f) 0.01 to 2 wt% of lubricant,
- (g) 0.5 to 10 wt% of co-solvent, and
- (h) 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, $(\text{NH}_4)_2\text{HPO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, NaH_2PO_4 , Na_2HPO_4 , phytic acid, glycolic acid, lactic acid, acetic acid, oxalic acid, and mixtures thereof.

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-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.

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 film former is one or more selected from the group consisting of polyurethane resin (cationic or non-ionic), acrylic emulsion (cationic or non-ionic), and mixtures thereof.

7. The solution composition of claim 1, wherein the lubricant is one or more selected from the group consisting of polytetrafluoroethylene (PTFE), polyethylene (PE), carnauba-based wax, and mixtures thereof.

8. 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.

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

10. A surface-treated steel sheet comprising:

10 a steel sheet; and
a coating layer formed on at least one surface of the steel sheet,
wherein the coating layer is formed of the composition of any one of claims 1 to 9.

11. The surface-treated steel sheet of claim 10, wherein the coating layer has a thickness of 0.2 to 3.0 μm .

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

providing a steel sheet;
applying the composition of any one of claims 1 to 9 on at least one surface of the steel sheet; and
heat-treating the steel sheet coated with the composition at 50 to 250°C.

20 13. The method of claim 12, wherein the steel sheet is a Zn-Al-Mg-based hot-dip galvanized steel sheet.

14. The method of claim 12, wherein the applying of the composition is carried out by one or more methods selected from bar coating, roll coating, spray coating and dipping coating methods.

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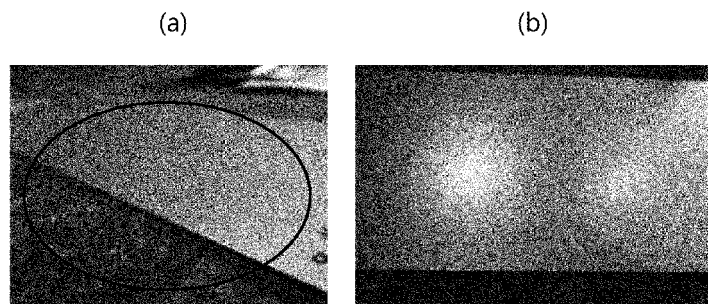


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/020821

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/06(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 22/06(2006.01); B05D 7/14(2006.01); C09D 1/02(2006.01); C09D 5/10(2006.01); C23C 22/00(2006.01);
C23C 22/07(2006.01); C23C 22/53(2006.01); C23C 22/78(2006.01); C23F 11/18(2006.01); C23F 3/00(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: 조성물(composition), 표면 처리(surface treating), 강판(steel sheet), 크롬(Cr), 실란(silane), 도금(plating), 코팅(coating)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	KR 10-2011-0083744 A (NIHON PARKERIZING CO., LTD.) 20 July 2011 (2011-07-20) See paragraphs [0132]-[0134].	1-14
A	CN 111876782 A (FUJIAN HUAIJIE ELECTRICAL TECHNOLOGY CO., LTD.) 03 November 2020 (2020-11-03) See paragraph [0028] and claims 1 and 3.	1-14
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A	KR 10-2015-0111676 A (PARK, Soon Hee) 06 October 2015 (2015-10-06) See paragraphs [0038]-[0039] and claim 1.	1-14

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

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Information on patent family members

International application No.

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