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(54) Title: RUSTPROOFING AGENT FOR ZINC PLATED STEEL SHEET

(57) **Abrégé/Abstract:**

A rustproofing agent for a zinc plated steel sheet is provided which contains (A) a chromium aqueous solution containing an organic substance and (B) an acid metal such as a metal salt of nitric acid or phosphoric acid. All of the chromium in the chromium aqueous solution of component A is trivalent chromium. It is preferable if the organic substance in component A contains at least one type of oxy acid or oxide thereof. The metal in the acid metal salt of component B is an alkaline earth metal, cobalt, nickel, iron, zirconium, titanium, etc. It is also preferable if (C) a water-dispersible silica is contained as an additional component. The present invention also provides a zinc plated steel sheet, in which at least one side of the surface of a zinc plated steel sheet is coated with the zinc plated steel sheet rustproofing agent and the rustproofing agent dried to form a coating with a dry coating weight of 0.01 to 3 g/m².



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(54) Title: RUSTPROOFING AGENT FOR ZINC PLATED STEEL SHEET

(57) Abstract: A rustproofing agent for a zinc plated steel sheet is provided which contains (A) a chromium aqueous solution containing an organic substance and (B) an acid metal such as a metal salt of nitric acid or phosphoric acid. All of the chromium in the chromium aqueous solution of component A is trivalent chromium. It is preferable if the organic substance in component A contains at least one type of oxy acid or oxide thereof. The metal in the acid metal salt of component B is an alkaline earth metal, cobalt, nickel, iron, zirconium, titanium, etc. It is also preferable if (C) a water-dispersible silica is contained as an additional component. The present invention also provides a zinc plated steel sheet, in which at least one side of the surface of a zinc plated steel sheet is coated with the zinc plated steel sheet rustproofing agent and the rustproofing agent dried to form a coating with a dry coating weight of 0.01 to 3 g/m².



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Rustproofing Agent for Zinc Plated Steel Sheet

Field of the Invention

The present invention relates to a rustproofing agent for zinc plated steel sheet, which contains no hexavalent chromium (a hazardous substance) whatsoever, and has excellent corrosion resistance, fingerprint resistance, and blackening resistance. The invention also relates to a zinc plated steel sheet that has undergone
5 a rustproofing treatment with this agent.

Discussion of the Related Art

Steel sheets used in the fabrication of consumer electrical products and for construction materials are often subjected to a chromating treatment for the purpose
10 of improving the corrosion resistance of the surface of zinc plated steel sheets. However, this chromating involves the use of hexavalent chromium, which is harmful to both the environment and humans. Consequently, there has been an urgent need in recent years for a chemical conversion treatment that does not make use of hexavalent chromium, and even for a chemical conversion treatment that does
15 not involve the use of chromium itself.

The methods discussed in Japanese Laid-Open Patent Applications 2000-054157 and H10-081976 are related to this type of chemical conversion treatment.

Japanese Laid-Open Patent Application 2000-054157 discloses a method related to a chemical conversion surface treatment agent that contains phosphorus, a
20 metal such as molybdenum, and trivalent chromium ions, but contains no hexavalent chromium or fluorides. With this method, the coating film weight must be at least 1 g/m² in order to achieve temporary rustproofing performance on a par with that of a chromating treatment, which is the conventional chemical conversion treatment (where the white rust occurs over less than 10% of the surface area after 72 hours of

saltwater spray at a chromium adhesion weight of 10 mg/m²). Moreover, this level of corrosion resistance can hardly be considered adequate, and it is difficult to achieve a level at which white rust occurs over less than 3% of the surface area after 120 hours of saltwater spray.

5 Japanese Laid-Open Patent Application H10-081976 discloses a method related to a chromating solution in which the percentage of hexavalent chromium is lowered to 0.1 or less as the proportion of hexavalent chromium/total chromium. With this method, the solution still contains hexavalent chromium, albeit very little, and the resulting corrosion resistance does not even reach the level of temporary
10 rustproofing.

Thus, as of now there has yet to be obtained a surface treated metal sheet having a coating that contains no hexavalent chromium whatsoever and that also has excellent corrosion resistance, electrical conductivity, and fingerprint resistance.

Summary of the Invention

15 The present invention was conceived in an effort to solve the problems encountered with the above prior art, and it is an object thereof to provide a treatment agent that contains no hexavalent chromium whatsoever and is used to form a coating that not only protects a zinc plated steel sheet against corrosion, but also has excellent blackening resistance and fingerprint resistance.

20 As a result of diligent search for a means for solving the above-mentioned problems encountered with prior art, the inventors discovered that these problems could be solved by using a zinc plated steel sheet rustproofing agent comprised of [i] a chromium aqueous solution containing an organic substance and [ii] an acid metal salt selected from the group consisting of nitric acid metal salts and phosphoric acid
25 metal salts.

Specifically, the present invention is a rustproofing agent for a zinc plated steel sheet, comprising (A) a chromium aqueous solution containing an organic substance and (B) an acid metal salt, and by all of the chromium in the chromium

aqueous solution of component A (as well as in the rust proofing agent as a whole) being trivalent chromium. It is preferable in the present invention if the organic substance in component A contains at least one type of oxy acid or oxide thereof. It is also preferable if the weight ratio of chromium in component A with respect to a total solids content of 100 wt% in the rustproofing agent (component A + component B) is 1 to 30 wt% calculated as metallic chromium. It is also preferable if the metal in the acid metal salt of component B is at least one selected from the group consisting of alkaline earth metals, cobalt, nickel, iron, zirconium, and titanium. It is also preferable if (C) a water-dispersible silica is contained as an additional component, and if the proportion of the solids content of component C with respect to a total solids content of 100 wt% in the rustproofing agent (component A + component B) is 5 to 50 wt%.

An alternative way in which the present invention may be described is as follows: A rustproofing agent for zinc plated steel sheet, comprising water, chromium, an organic substance and an acid metal salt selected from the group consisting of nitric acid metal salts, phosphoric acid metal salts and mixtures thereof, wherein all of the chromium in the rustproofing agent is trivalent chromium.

The present invention is further a zinc plated steel sheet, in which at least one side of the surface of a zinc plated steel sheet is coated with the above-mentioned zinc plated steel sheet rustproofing agent, and this coating is dried to form a coating with a dry coating weight of preferably 0.01 to 3 g/m².

Detailed Description of the Invention

Component A of the zinc plated steel sheet rustproofing agent of the present invention is a chromium aqueous solution containing an organic substance, with all of the chromium in this chromium aqueous solution being trivalent chromium. This component A can be prepared, for example, by a method in which an organic substance is added to an aqueous solution of hexavalent chromium in an excess amount over the amount needed to reduce all of the hexavalent chromium to

trivalent chromium, or by a method in which an organic substance is mixed with at least one trivalent chromium compound selected from among chromium biphosphate, chromium fluoride, and chromium nitrate.

5 There are no particular restrictions on the organic substance, but examples include carboxylic acids (such as formic acid, acetic acid, propionic acid, butyric acid, and other saturated fatty acids, and acrylic acid, crotonic acid, isocrotonic acid, and oleic acid), oxy (i.e., hydroxy-substituted) acids (such as glycolic acid, lactic acid, hydroacrylic acid, α -hydroxybutyric acid, glyceric acid, tartronic acid, malic acid, tartaric acid, citric acid, and gallic acid), alcohols (such as methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol), sugars (such as fructose, sucrose, 10 and glucose), and oxides of these. The term "oxides" is used herein to mean oxidation products of the aforementioned organic substances which still retain an organic character (i.e., where the organic substance has not been completely oxidized to carbon dioxide and water). Such oxides will typically be generated when an 15 organic substance is combined with hexavalent chromium in an amount which is in excess relative to the amount theoretically required to reduce all of the hexavalent chromium to trivalent chromium. Oxy acids and oxides thereof are preferred, and it is preferable for at least one type of these to be contained in the rustproofing agent. There are no particular restrictions on the mixing ratio when two or more types of 20 organic substance are used. The organic substance is added in an excess amount over the amount needed to maintain a state in which all of the chromium present in component A is reduced to trivalent chromium.

The weight ratio of chromium in component A with respect to a total solids content of 100 wt% in the rustproofing agent (component A + component B) is 25 preferably 1 to 30 wt% calculated as metallic chromium, with 2 to 25% being even better, and 3 to 20% being particularly favorable. The level of corrosion resistance will be unacceptable if the weight ratio of chromium in component A with respect to a total solids content of 100 wt% in the rustproofing agent is either less than 1 wt% or over 30 wt%.

There are no particular restrictions on the acid metal salt used as component B in the present invention, but it is preferable to use a salt of nitric acid and at least one type of metal selected from the group consisting of alkaline earth metals such as magnesium, calcium, strontium, and barium, and cobalt, nickel, iron, zirconium, and titanium. Component B is preferably added to the rustproofing agent of the present invention in the form of an aqueous solution. There are no particular restrictions on the amount added, but preferably it is 10 to 90 wt%, and even more preferably 20 to 70 wt%, with respect to a total solids content of 100 wt% in component B. Adding a nitric acid metal salt improves the corrosion resistance and blackening resistance. Examples of metal salts other than a nitric acid metal salt include sulfuric acid metal salts and metal halides, but since it is known that sulfuric acid radicals and halides generally accelerate the corrosion of metals, the use of these metal salts is undesirable. Other examples of metal salts are phosphoric acid metal salts. It is commonly known that these metal salts have an anticorrosive effect, and there are cases when a further increase in corrosion resistance is needed beyond what can be accomplished using a nitric acid metal salt alone, in which case a phosphoric acid metal salt can be added to the rustproofing agent of the present invention as well. Phosphoric acid metal salts by themselves (i.e., without any other type of acid metal salt) may also be utilized.

The order in which the components A and B are prepared and combined is not critical to the performance of the rustproofing agent. For example, the chromium aqueous solution may first be prepared and the acid metal salt thereafter added. Alternatively, the acid metal salt may be present together in solution with the chromium compound and/or organic substances before the chromium compound and the organic substance are combined.

Water-dispersible silica (C) can be contained as an additional component in the zinc plated steel sheet rustproofing agent of the present invention. Adding this component C results in even better corrosion resistance. Water-dispersible silicas include colloidal silica and vapor phase silica. There are no particular restrictions on the colloidal silica, but examples include Snow-Tex C, Snow-Tex O, Snow-Tex N, Snow-Tex S, Snow-Tex UP, Snow-Tex PS-M, Snow-Tex PS-L, Snow-Tex 20,

Snow-Tex 30, and Snow-Tex 40 (all made by Nissan Chemical Industries). There are no particular restrictions on the vapor phase silica which may be used, but examples include Aerosil 50, Aerosil 130, Aerosil 200, Aerosil 300, Aerosil 380, Aerosil TT600, Aerosil MOX80, and Aerosil MOS170 (all made by Nippon Aerosil).

The amount in which the above-mentioned component C is added, as solids, is preferably 5 to 50 wt% with respect to a total solids content of 100 wt% in the rustproofing agent (component A + component B), with 10 to 45 wt% being even better, and 15 to 40 wt% being particularly favorable. There will be little improvement in corrosion resistance under 5 wt%, but exceeding 50 wt% is undesirable from a cost standpoint because no significant further improvement in corrosion resistance is achieved. Generally speaking, it will be preferred to add component C after components A and B have been combined and after any pH adjustment has been performed since otherwise the stability of the water-dispersible silica may be adversely affected.

Also, an acid component or alkali component can be added to the zinc plated steel sheet rustproofing agent of the present invention. There are no particular restrictions on the acid component, but examples include hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid. Neither are there any particular restrictions on the alkali component, but examples include aqueous ammonia and amines. There are no particular restrictions on the pH after these components have been added.

The zinc plated steel sheet of the present invention is obtained by coating at least one surface of a zinc plated steel sheet with the zinc plated steel sheet rustproofing agent of the present invention to form a wet coating of the rustproofing agent on said surface, and then drying this wet coating to form a dry coating with a coating weight of 0.01 to 3 g/m². It is undesirable for the dry coating weight to be less than 0.01 g/m² because the corrosion resistance will be inadequate. On the other hand, a dry coating weight that exceeds 3 g/m² is not cost effective because there will be no further improvement in corrosion resistance.

Examples of the zinc plated steel sheet used in the present invention include electrogalvanized steel sheet, hot galvanized steel sheet, alloyed hot galvanized steel sheet, 5% aluminum-containing hot galvanized steel sheet, and 55% aluminum-containing hot galvanized steel sheet. The zinc plated on the steel sheet thus may be a zinc alloy. The surface of the zinc plated steel sheet is preferably subjected to alkaline degreasing, acid washing, or some other cleaning before being coated with the rustproofing agent of the present invention and then dried.

There are no particular restrictions on the method for applying the zinc plated steel sheet rustproofing agent of the present invention, but roll coating, dipping, electrostatic coating, or another such method can be used. It is preferable for the coating to be dried at a final sheet temperature of 50 to 200°C.

A resin coating can also be applied over a metal sheet that has been surface treated with the zinc plated steel sheet rustproofing agent of the present invention in order to further enhance corrosion resistance, prevent scratching, and so on. There are no particular restrictions on the resin coating applied here, but it is favorable to apply a surface treatment agent whose main component is an acrylic resin, urethane resin, epoxy resin, polyester resin, or the like, and it is preferable for the resin coating weight to be between 0.5 and 10 g/m² (dry weight).

Examples

The present invention will now be described in specific terms through examples and comparative examples. These examples are only given for the purpose of describing the present invention, and do not serve to limit the present invention in any way.

Production of test sheet

(1) Test materials

The following commercially available materials were used as test materials.

- Electrogalvanized steel sheet (EG)

5 thickness: 0.8 mm, plating basis weight: 20/20 (g/m²)

- Hot galvanized steel sheet (GI)

 thickness: 0.8 mm, plating basis weight: 60/60 (g/m²)

- 5% aluminum-containing hot galvanized steel sheet (GF)

 thickness: 0.8 mm, plating basis weight: 90/90 (g/m²)

10 (2) Degreasing

Each of the above test materials was degreased with a silicate-based alkali degreaser called FINE CLEANER 4336 (trade name of Nihon Parkerizing) (concentration: 20 g/L, temperature: 60°C, 20 seconds of spraying), after which the material was rinsed with tap water.

15 (3) Preparation of the zinc plated steel sheet rustproofing agent of the present invention

20 A chromium aqueous solution containing the organic substance(s) shown in Table 1 (solids concentration: 10 wt%), the nitric acid metal salt aqueous solution shown in Table 2, and the water-dispersible silica shown in Table 3 were added in that order at room temperature to distilled water. The components were mixed while being stirred with a propeller stirrer to prepare an aqueous metal surface treatment agent. The zinc plated steel sheet rustproofing agents of the examples (solids concentration: 10 wt%) are shown in Table 4, while the rustproofing agents of the

comparative examples (solids concentration: 10 wt%) are shown in Table 5.

Table 1

No.	Organic substance ^{*1}	Cr ³⁺ /total Cr	Solids concentration	Cr concentration ^{*2}	Remarks
A1	tartaric acid/formic acid	100%	20%	20%	
A2	lactic acid/sucrose	100%	20%	15%	
A3	lactic acid	100%	25%	10%	
A4	tartaric acid/formic acid/lactic acid	100%	15%	25%	
A5	none	100%	10%	15%	no organic substance
A6	lactic acid/formic acid	30%	10%	50%	contains hexavalent Cr

*1: Organic substances were mixed in equal amounts by weight.

*2: Concentration calculated for metallic chromium versus solids weight.

Table 2

No.	Compound	Solids concentration
B1	cobalt nitrate aqueous solution	10%
B2	calcium nitrate aqueous solution	10%
B3	zinc nitrate aqueous solution	10%

Table 3

No.	Compound	Solids concentration
C1	Snow-Tex O	20%
C2	aqueous dispersion of Aerosil 200	10%

Table 4

No.	Solids concentration of zinc plated steel sheet rustproofing agent ^{*3}			Chromium weight ratio ^{*4}	Water-dispersible silica ^{*5}
	Component A	Component B	Component C		
1	A1(70)	B1(30)	none	14.0%	none
2	A2(70)	B1(30)	none	10.5%	none
3	A3(60)	B1(40)	none	6.0%	none
4	A4(80)	B1(20)	none	20.0%	none
5	A2(50)	B2(50)	none	7.5%	none
6	A3(60)	B3(40)	none	6.0%	none
7	A1(60)	B1(20)	C1(20)	15.0%	25.0%
8	A1(80)	B1(10)	C2(10)	17.8%	11.1%
9	A4(93)	B1(2)	C1(5)	24.5%	5.3%
10	A1(50)	B1(20)	C1(30)	14.3%	42.8%
11	A4(15)	B1(25)	C1(60)	3.8%	150.0%
12	A1(60)	B1(10)	C1(30)	17.1%	42.8%

*3: The numbers in parentheses indicate the solids weight percentage with respect to a total solids content of 100 wt% in the zinc plated steel sheet rustproofing agent.

*4: Weight ratio of chromium (calculated as metallic chromium) in component A versus the solids weight of components A + B

*5: Solids ratio of component C versus the solids weight of components A + B

Table 5

No.	Solids concentration of rustproofing agent ^{*6}		Chromium weight ratio ^{*4}	Water-dispersible silica ^{*5}	Reason
	Component A	Component B			
13	A5(70)	B1(30)	10.5%	none	no organic substance
14	A6(70)	B1(30)	35.0%	none	contains hexavalent Cr
15	A3(100)	none	10.0%	none	no nitric acid metal salt

*6: The numbers in parentheses indicate the solids weight percentage with respect to a total solids content of 100 wt% in the rustproofing agent.

(4) Application of zinc plated steel sheet rustproofing agent

Each of the various zinc plated steel sheet rustproofing agents prepared above was used to coat each of the above-mentioned test sheets with a bar coater, and the coating was dried at an atmosphere temperature of 240°C. The coating weight (g/m²) was adjusted by suitably adjusting the solids concentration of the aqueous metal surface treatment agent.

Corrosion resistance test for flat parts

A saltwater spray test was conducted according to JIS Z 2371, lasting 120 hours for the EG and GI materials, and 168 hours for the GF material. The sheets were examined for white rust and evaluated according to the following criteria.

10 Evaluation criteria

⊙: white rust occurred in less than 3% of the total surface area

○: white rust occurred in at least 3% but less than 10% of total surface area

△: white rust occurred in at least 10% but less than 30% of total surface area

×: white rust occurred in at least 30% of total surface area

15

Fingerprint resistance test

The color tone (L, a, and b values) of the test sheets was measured by colorimeter (ZE-2000, made by Nippon Denshoku), after which each sheet was coated with petrolatum and then wiped off, the color tone was measured again with a colorimeter, and the difference in the color tone (ΔE) was used to make an evaluation based on the criteria below.

$$\Delta E = ((L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2)^{0.5}$$

Where L_1 , a_1 , and b_1 are the values prior to petrolatum coating, and L_2 , a_2 , and b_2 are the values after petrolatum coating.

Evaluation criteria

- 5 ⊙: ΔE is less than 2
- : ΔE is at least 2 but less than 3
- Δ: ΔE is at least 3 but less than 5
- ×: ΔE is at least 5

Blackening resistance test

- 10 A test sheet was left for 24 hours in an atmosphere with a humidity of 90%, and the L values were measured before and after the test. The difference in L values (ΔL) was used to make an evaluation based on the criteria below.

Evaluation criteria

- ⊙: ΔL is less than 1
- 15 ○: ΔL is at least 1 but less than 3
- Δ: ΔL is at least 3 but less than 5
- ×: ΔL is at least 5

- 20 Table 6 gives the test results for the examples of the present invention, while Table 7 gives the test results for the comparative examples. In Examples 1 to 19, in which the zinc plated steel sheet rustproofing agent of the present invention was

used, the results for corrosion resistance, fingerprint resistance, and blackening resistance were all good. On the other hand, in Comparative Examples 1 and 3, in which a rustproofing agent outside the range of the present invention was used, the results for corrosion resistance, fingerprint resistance, and blackening resistance were all inferior. Comparative Example 2 is different in basic concept from the present invention in that hexavalent chromium is contained, which is harmful to humans and the environment.

Table 6

No.	Material	Aqueous metal surface treatment agent		Final sheet temp. (°C)	Coating performance		
		Type	Coating weight* ² (g/m ²)		Corrosion resistance	Fingerprint resistance	Blackening resistance
1	EG	1	0.5	80	⊙	○	⊙
2	G1	2	0.5	80	⊙	○	⊙
3	GF	3	0.5	80	⊙	○	⊙
4	EG	4	0.5	80	⊙	○	⊙
5	G1	5	0.5	80	⊙	○	⊙
6	GF	6	0.5	80	⊙	○	⊙
7	EG	7	0.5	80	⊙	⊙	⊙
8	G1	8	0.5	80	⊙	⊙	⊙
9	GF	9	0.5	80	⊙	⊙	⊙
10	EG	10	0.5	80	⊙	⊙	⊙
11	G1	11	0.5	80	⊙	⊙	⊙
12	GF	12	0.5	80	⊙	⊙	⊙
13	EG	1	0.02	80	○	○	○
14	G1	1	0.1	80	○	○	○
15	GF	1	1.0	80	⊙	○	⊙
16	EG	1	3.0	80	⊙	○	⊙
17	G1	1	0.5	60	⊙	○	⊙
18	GF	1	0.5	100	⊙	○	⊙
19	G1	1	0.5	150	⊙	○	⊙

Table 7

No.	Material	Aqueous metal surface treatment agent		Final sheet temp. (°C)	Coating performance		
		Type	Coating weight* ² (g/m ²)		Corrosion resistance	Fingerprint resistance	Blackening resistance
1	EG	13	0.5	80	△	×	×
2	G1	14	0.5	80	⊙	○	○
3	GF	15	0.5	80	×	○	×

As described above, a coating film formed by coating a zinc plated steel sheet with the zinc plated steel sheet rustproofing agent of the present invention and then drying has excellent corrosion resistance, fingerprint resistance, and blackening resistance, and because it contains no hexavalent chromium that would be harmful to humans and the environment, it has tremendous industrial utility value.

What is claimed is:

1. A rustproofing agent for zinc plated steel sheet, comprising
 - (A) an aqueous solution comprising chromium and an organic substance, wherein all of the chromium in the aqueous solution is trivalent chromium; and
 - (B) at least one acid metal salt selected from the group consisting of nitric acid metal salts and phosphoric acid metal salts.
2. The rustproofing agent of claim 1 wherein the organic substance is selected from the group consisting of oxy acids, oxides of oxy acids and mixtures thereof.
3. The rustproofing agent according to Claim 1 or 2, wherein chromium (calculated or metallic chromium) is present in (A) in an amount from 1 to 30 wt% relative to a total solids content in (A) and (B) combined of 100 wt%.
4. The rustproofing agent of any of claims 1, 2 or 3, wherein the metal in the acid metal salt is selected from the group consisting of alkaline earth metals, cobalt, nickel, iron, zirconium, and titanium.
5. The rustproofing agent of any of claims 1, 2, 3 or 4, additionally comprising a water-dispersible silica.
6. The rustproofing agent of claim 5, wherein said water-dispersible silica is present in an amount of from 5 to 50 wt% relative to a total solids content in (A) and (B) combined of 100 wt%.

- 5 7. A method of rustproofing a zinc plated steel sheet comprising contacting at least one surface of said zinc plated steel sheet with the rustproofing agent according to any of claims 1 to 6 to form a wet coating of the rustproofing agent on said surface and drying said wet coating to form a dry coating with a coating weight of weight of 0.01 to 3 g/m².