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[54] **METHOD FOR SURFACE TREATMENT OF ZINC-PLATED SHEET STEEL**
7 Claims, No Drawings

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[56] **References Cited**

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ABSTRACT: Method of the surface treatment of zinc-plated sheet steel, wherein cathodic electrolysis of the surface of zinc-plated sheet steel is provided as a pretreatment of the surface treatment with chromic acid of said zinc-plated sheet steel, for the prevention of white rust.

METHOD FOR SURFACE TREATMENT OF ZINC-PLATED SHEET STEEL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates in general to the method of the surface treatment of zinc-plated sheet steel, and more particularly to a novel method for the surface treatment of hot dipping zinc-plated sheet steel for the prevention of white rust.

2. Description of the Prior Art

To gather white rust on the surface easily during storage and transportation, is the trouble with zinc-plated sheet steel; and in order to prevent the rust, there is generally carried out a simple rust prevention method according to which such steel is treated in a treating bath consisting mainly of chromic acid, so as to form chromate film on the surface. However, this conventional method is not effective enough in such humid areas as Japan; even the treated steel gathers white rust, that is, the prevention of the rust is difficult. The formation of white rust is the main reason of complaints about zinc-plated sheet steel.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a method for the surface treatment of zinc-plated sheet steel, as an improvement of the conventional method for the prevention of white rust formation on the surface of zinc-plated sheet steel, according to which improvement the treatment is simple and yet effective in the prevention of white rust formation during handling and storage, even in humid areas.

Another object of the present invention is to provide a pretreatment method to the conventional method for the surface treatment of zinc-plated sheet steel with chromic acid for the prevention of white rust formation, such pretreatment method making the surface treatment perfectly effective and yet being operated in a short time and easily.

In order to attain these objects, the method of the present invention is so practised that in treating hot dipped zinc-plated sheet steel by immersion or electrolysis in a treating bath containing chromic acid alone or as the main ingredient for the prevention of white rust, cathodic electrolysis of the surface of said sheet steel is carried out in a diluted aqueous solution of such stable neutral salts as KCl, NaCl, $(NH_4)_2CO_3$, $(NH_4)_2CrO_4$ and $(NH_4)_2CrO_7$, as the pretreatment for increasing the effect of the above treatment, thereby activating and reducing the surface of said steel by having the zinc oxide film covering the surface reduced to be removed.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Having studied minutely the reaction of chromic acid with the surface of zinc-plated sheet steel in the said treatment with chromic acid, the inventors discovered a 1,000 A. thick film of such zinc compounds as basic zinc carbonate covering the surface of hot dipped zinc-plated sheet steel on the market and hindering the above reaction with chromic acid.

Regarding such film, studies were carried out widely in the fields concerned, but there were presented no findings until the inventors of the present invention attained, through analysis of electronic diffractions, a finding that such harmful film consists mainly of basic zinc carbonate and noncrystalline zinc oxide. Based on this finding, the inventors tried a variety of methods for the removal of oxides from the surface of hot dipped zinc-plated sheet steel, and have found that if cathodic electrolysis is provided to the treatment with chromic acid so as to remove the above-mentioned oxides with scarce change to the appearance of the surface, even the conventional chromate treatment using the simple process of immersion can produce, uniformly over the surface and efficiently, a chromate film better in white rust prevention than that made by only the treatment with chromic acid but without this pretreatment according to the conventional method.

The present invention is characterized by subjecting the surface of hot dipped zinc-plated sheet steel to cathodic electrolysis in an aqueous solution of at least one kind selected from a group of such stable neutral salts as KCl, NaCl $(NH_4)_2CO_3$, $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$, as the pretreatment of the publicly known chromate treatment by immersion or electrolysis.

Said electrolysis, as a pretreating step, is carried out in an aqueous solution of such stable neutral salts as KCl, $(NH_4)_2CO_3$ and $(NH_4)_2Cr_2O_7$, as mentioned above, with comparatively diluted concentration with a pH value of about 6 to 10, using the hot dipped zinc-plated sheet steel as cathode, at a current density of less than 50 A./dm.^{2}, more preferably 1 to 25 A./dm.^{2} for such a short time of 1 second; it is to activate and reduce the surface with scarce change to the appearance, thereby efficiently reducing and removing zinc oxide and other materials covering the surface of steel as mentioned above.

When using pretreatment according to the present invention, the reaction of chromic acid with the surface of the steel is greatly promoted, making even the conventional chromate treatment, using the simple immersion done subsequently, useful in the production of a chromate film effective for the prevention of white rust formation in humid areas, as mentioned below in examples; even better results could be obtained in the prevention of white rust with a chromate film produced by the more elaborate process of electrolysis used for the conventional chromate treatment.

The reason that, according to the present invention, cathodic electrolysis is used for the removal of oxide film from the surface of zinc-plated sheet steel, as mentioned above, and that the electrolyte used for such electrolysis is limited in pH value to a range from 6 to 10, is explained in comparison with other methods, as follows:

The above removal of oxide film from the surface of zinc-plated sheet steel makes it easy to carry out the chromate treatment done posterior to the removal, and the treated steel is greatly improved in the corrosion resistance and the white rust prevention of the surface zinc.

When considering the removal of oxide film from the surface zinc from a general viewpoint, the simplest and easiest process is to dissolve away such oxide film chemically, and that can be done effectively by using a highly acidic solution of low pH value, or, on the contrary, a highly alkaline solution of high pH value, when the following reactions take place:

$$pH<4: ZnO+2H^+ \rightarrow Zn^+ + H_2O$$

$$pH<12: ZnO+OH^- \rightarrow HZnO_2^-$$

In these cases, zinc oxide film is dissolved away in the state of ion.

However, with such pH values as mentioned above, metallic zinc also dissolves easily; therefore, with the above pH values, that is, when using a solution of HCl or NaOH, the oxide film on the surface zinc dissolves away, but troubles are that the so-exposed metallic zinc also dissolves, thus the zinc plating layer is damaged and zinc ions accumulate in the solution. Because of such troubles, the use of acid or alkali for the removal of oxide film is not recommendable. Another trouble is that if such treatment is carried out continuously, a part of acidic or alkaline solution is mixed with a chromic acid treating solution, causing undesirable results.

When using cathodic electrolysis according to the present invention, the oxide film can be removed effectively without such troubles. By reduction by such electrolysis, oxide and basic zinc carbonate film can be removed. As for the so-exposed surface zinc, it does not dissolve, as it is held with anode and the solution is limited in pH value to a range of 6 to 10. The noteworthy merit of this process is that the oxide film covering the surface is removed without damaging the zinc plating layer.

As mentioned above, the electrolyte should not be strongly corrosive, as the surface metal has been exposed as a result of the reduction made by the electrolysis for the removal of the oxide film. Taking this point into consideration, pH value of the electrolyte is desirable to be in a range of 6 to 10, so that the metallic zinc is dissolved with difficulty. For making such electrolyte, a solution made of such a substance as KCl, NaCl,

$(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$, which makes a pH value of 6 to 10, in water is used, Again regarding the limitation of pH value to maximum of 10, it is because zinc in a solution of a pH value of more than 10 is apt to turn into the passive state; therefore, oxide film forms again during the period between reduction by electrolysis and rinsing the water; hence the pH value of an electrolyte effective for the removal of oxide film from the surface zinc by the reduction made by cathodic electrolysis is preferred to be between 6 to 10. Moreover, electrolysis in a solution of the pH value within this range, can be carried out successfully at the current efficiency of 100 percent without generation of hydrogen.

Regarding the treatment with chromic acid which is to be used in combination with the pretreatment according to the present invention, no explanation of it is given, as it is publicly known. However, it should be noted that both immersion and electrolysis can be applied to the above treatment; also use of any of a treating bath containing chromic acid or as a main ingredient or a bath containing chromic acid plus such other substances as silica gel for the above treatment can be expected to bring about satisfactory results as mentioned below.

The following examples 1–4 show the comparison in corrosion resistance after the same treatment with chromic acid between the samples of hot dipped zinc-plated sheet steel with oxide film left unremoved and those of the same specifications but removed of oxide film by the pretreatment according to the present invention.

EXAMPLE 1

The removal of oxide film was carried out by cathodic electrolysis according to the present invention, with the following conditions:

1. Electrodes:	Cathode: Hot dipped zinc-plated sheet steel Anode: Carbon plate
2. Electrolyte:	0.1 N ammonium carbonate solution
3. Current density:	5 A./dm.²
4. Operation time:	1–2 seconds
5. Temperature:	Room temperature

Table 1 shows the comparison in corrosion resistance after the treatments, using an aqueous solution of chromic acid alone and a bath containing chromic acid as the main ingredient, between the samples previously removed of oxide film according to the present invention and those of the same specifications but with oxide film left unremoved.

EXAMPLE 2

Cathodic electrolysis according to the present invention was carried out under the following conditions:

1. Electrodes:	Same as mentioned in example 1.
2. Electrolyte:	0.1 N ammonium bichromate solution.
3. Current density:	20 A./dm.²
4. Operation time:	1–2 seconds
5. Temperature:	25° C.

EXAMPLE 3

1. Electrodes	Same as mentioned in example 1.
2. Electrolyte:	1 N ammonium carbonate solution
3. Current density:	10 A./dm.²
4. Operation time:	1 second
5. Temperature:	40° C.

EXAMPLE 4

When treated with an aqueous solution of chromic compounds (an electrolyte requiring no water rinsing)

1. Electrodes:	Anode: Stainless steel plate Cathode: Hot dipped zinc-plated sheet steel
2. Electrolyte:	0.1 N ammonium bichromate 0.1 N chromate anhydride
3. Current density:	10 A/dm²
4. Operation time:	1 second
5. Temperature:	50° C.

TABLE 1.—COMPARISON IN CORROSION RESISTANCE

Sample No.	Pretreatment	Chromic acid treatment	Chromium deposited (mg./m.²)	White rust (area percent) produced by brine spray tests after— 24 hrs.	48 hrs.	72 hrs.	96 hrs.
1 (Con.)	No	Immersed in aqueous solution of chromic acid alone.	8	50	100	100	100
1 E (PI)	Reduction by electrolysis		9	No change	No change	5	20
2 (Con.)	No	Immersed in bath containing chromic acid as main ingredient.	10	do	80	100	100
2 E (PI)	Reduction by electrolysis		12	do	No change	No change	5

Remarks: (1) Bath containing chromic acid (2 and 2E): Chromic anhydride 5 g./l., colloidal silica 20 g./l., water rest, solution temperature 25° C.
(2) Con.=By conventional method; PI=According to the present invention.

TABLE 2.—COMPARISON IN CORROSION RESISTANCE

Sample No.	Pretreatment	Chromic acid treatment	Chromium deposited (mg./m.²)	White rust (area percent) produced by brine spray tests after— 24 hrs.	48 hrs.	72 hrs.	96 hrs.
1 (Con.)	No	Immersed in aqueous solution of chromic acid alone.	8	50	100	100	100
1 E (PI)	Reduction by electrolysis		10	No change	No change	5	10
2 (Con.)	No	Immersed in bath containing chromic acid as main ingredient.	16	5	100	100	100
2 E (PI)	Reduction by electrolysis		14	No change	No change	No change	5

Remarks: (1) Bath containing chromic acid (2 and 2E): Same as mentioned in Example 1. (2) Con.=By conventional method; PI=According to the present invention.

TABLE 3

Sample No.	Pretreatment	Chromic acid treatment	Total Cr deposited	White rust (area percent) produced by brine spray tests after— 24 hrs.	48 hrs.
1 (Con.)	No	Immersed in aqueous solution of chromic acid as main ingredient squeeze roll.	10 mg./m.²	No change	20.
1 E (PI)	Electrolysis		10 mg./m.²	do	No change.

Remarks: (1) Bath containing chromic acid (2 and 2E): Same as mentioned in Example 1. (2) Con.=By conventional method; PI=According to the present invention.

TABLE 4

Sample No.	Pretreatment	Electrolyte for pretreatment	Chromic acid treatment	Total Cr deposited	White rust (area percent) produced by brine spray tests after – 24 hrs.	48 hrs.
1 (Con.)	No		1% chromate anhydride aqueous solution (squeeze roll).	8 mg./m.²	50	100.
1 E (PI)	Electrolysis	0.1 N chromate anhydride		8 mg./m.²	No change	10.
2 (Con.)	No		Aqueous solution containing chromate as main ingredient (squeeze roll).	10 mg./m.²	do	20.
2 E (PI)	Electrolysis	0.1 N ammonium bichromate		10 mg./m.²	do	No change.

Remarks: (1) Bath containing chromic acid (2 and 2E): Same as mentioned in Example 1. (2) Con.=By conventional method; PI=According to the present invention. (3) When using this pre-treatment according to the present invention, the treatment with chromic acid can be given immediately that is, not through water rinsing.

As shown in examples 1, 2, 3 and 4, the removal of oxide film according to the present invention prior to the treatment with chromic acid, greatly improves the corrosion resistance of zinc-plated sheet steel.

What we claim is:

1. In the surface treatment of a zinc-plated sheet steel with chromic acid in forming chromate film on the surface for the prevention of white rust formation wherein the said treatment is preceded by a pretreating process, the improvement according to which said pretreating process comprises a preliminary treatment by cathode electrolysis of the surface of the zinc-plated steel sheet in an electrolytic solution made of a diluted water solution of a stable neutral salt.

2. The method according to claim 1 wherein said cathodic electrolysis is carried out in a diluted aqueous solution of at least one stable neutral salt selected from the group consisting of KCl, NaCl $(NH_4)_2CO_3$, $(NH_4)_2CrO_4$ and $(NH_4)_2Cr_2O_7$.

3. The method according to claim 1 wherein said cathodic electrolysis is carried out in an electrolyte of the pH value ranging from 6 to 10.

4. The method according to claim 1 wherein said cathodic electrolysis is carried out in the electrolyte of the pH value ranging from 6 to 10 and at a current density of 5 to 20 A./dm.² for a period of 1 to 2 seconds.

5. The method according to claim 1 wherein the surface treatment with chromic acid is carried out in a aqueous solution either of chromic acid alone or containing it as the main ingredient.

6. The method according to claim 1 wherein the surface treatment with chromic acid is carried out by immersion.

7. The method according to claim 1 wherein the surface treatment with chromic acid is carried out by electrolysis.

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