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(54) Method for producing chromate-treated plate steel material.

(57) According to the present invention, it is possible to produce a chromate-treated plated steel material which achieves an improved appearance thereof, particularly the minimization of a yellow tint peculiar to chromate, and enhanced corrosion resistance simultaneously and at a lower cost, which has been difficult with a prior art.

There is provided a method for producing a chromate-treated plated steel material, comprising the steps of

applying on at least one surface of a zinc- or zinc alloy-plated steel material a solution containing 1 to 15% by weight of chromic acid and/or reduced products of chromic acid having trivalent chromium and hexavalent chromium in the proportion of 1/2 to 1/1 by weight as the total amount of metal chromium, colloidal silica, calculated as SiO_2, in the proportion of 1/2 to 6/1 of the total weight of chromium, and further 0.1 to 10% by weight of at least one selected from the group consisting of carboxylic acids and/or derivatives thereof, which are stable in said solution,

heating and baking said chromate-treated steel material at a temperature ranging from 150 ° C to 300 ° C to form a chromate film having hexavalent chromium on the surface thereof in the proportion of 20% or less of the total weight of chromium and having a deposit of 10 to 150 mg/m^2 calculated as chromium.

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FIELD OF THE INVENTION

The present invention relates to a method for producing a chromate-treated zinc- or zinc alloy-plated steel material having improved corrosion resistance.

BACKGROUND OF THE INVENTION

Various chromate treatment methods have been implemented and practiced as a prior art treatment method for providing corrosion resistance to zinc- or zinc alloy-plated steel materials. Among the methods, a chromate treatment method wherein colloidal silica and trivalent chromium ion are added to a chromate solution is widely known as a method for providing high corrosion resistance (such as disclosed in Japanese Patent Publication Nos.42-14050 and 52-2851).

A chromate solution for improving the adherence and corrosion resistance of the steel material of the prior arts is disclosed in Japanese Patent Publication No.61-58552.

However, chromate-treated steel strips produced by these methods have a disadvantage that chromium is eluted upon alkali degreasing after the process of pressing. Moreover, these chromate-treated steel strips are directly and increasingly used in home electric appliances, furniture and auto parts recently, and these users now attach importance to the aesthetic appearance of these articles. However, it has been discovered that chromate-treated steel strips produced by these methods have a strong yellow tint which is peculiar to chromate and accordingly, are totally unsatisfactory.

A method for minimizing the elution of chromium, one of these drawbacks, is disclosed in Japanese Patent Kokai (Laid-open) No.63-137180, but it is still unsatisfactory in the improvement of the appearance. To overcome this drawback, the present inventors have disclosed in Japanese Patent Kokai No. 03-68783 a method for drying a steel strip at a temperature of 220°C or more after applying a chromate solution containing phosphate and silica.

This high-temperature drying method can provide satisfactory performance to chromate-treated steel strips, but has a drawback that it requires additional equipment for drying at high temperatures with the result of a great load on productivity and cost.

The prior art method for applying a chromate solution prepared by adding colloidal silica and trivalent chromium (hereinafter referred to as "Cr^{3+}") to a chromic acid to a plated steel strip, heating the strip to a temperature of 40 - 150°C to dry it provides almost required corrosion resistance and adherence to plated steel strips, but it cannot improve to satisfactorily reduce the elution of chromium, and provides an undesirable appearance particularly due to a strong yellow tint peculiar to chromate.

A treatment method disclosed in Japanese Patent Kokai No.03-68783 which eliminates these drawbacks has a disadvantage that it has lower productivity and higher cost than the prior arts.

The present inventors discovered that it is necessary to reduce the amount of Cr^{6+} remaining on the surface of a steel strip which is dried at a temperature of 220°C or more after the application of a chromate solution containing silica to 30% or less of the total amount of chromium in order to improve the corrosion resistance and appearance of the strip and minimize the elution of chromium in the strip. We applied for a patent as Japanese Patent Application No.01-204346 already laid-open in Kokai No. 03-68783. However, this high-temperature drying method has a great load on productivity and cost.

SUMMARY OF THE INVENTION

In view of the drawbacks with the prior arts, it is an object of the present invention to provide a method for producing at a low cost a chromate-treated plated steel material having excellent corrosion resistance and a weakened yellow tint peculiar to chromate due to prevention of chromium from being eluted.

To achieve this object, the present inventors have studied various additives which can reduce the amount of CR^{6+} remaining on the surface of the steel strip to 30% or less even when the strip is dried at lower temperatures after the application of the chromate solution. As a result, we have discovered that carboxylic acids and/or derivatives thereof, whose examples will be illustrated later, act on Cr^{+6} as a reducing agent when the strip is dried, and that these additives can also effectively improve corrosion resistance by increasing the thickness of a chromate film. The present invention is completed upon this discovery.

Namely, to achieve the aforementioned object, according to the present invention, there is provided a method for producing a chromate-treated plated steel material, comprising the steps of

applying on at least one surface of a zinc- or zinc alloy-plated steel material a solution containing 1 to 15% by weight of chromic acid and/or reduced products of chromic acid having trivalent chromium and hexavalent chromium in the proportion of 1/2 to 1/1 by weight as the total amount of metal chromium, colloidal silica, calculated as SiO_2, in the proportion of 1/2 to 6/1 of the total weight of chromium, and further 0.1 to 10% by weight of at least one selected from the group consisting of carboxylic acids and/or derivatives thereof, which are stable in said solution,

heating and baking said chromate-treated steel material at a temperature ranging from 150°C to 300°C to form a chromate film having hexavalent chromium on the surface thereof in the proportion of 20% or less of the total weight of chromium and having a deposit of 10 to 150 mg/m^2 calculated as chromium.

Preferable carboxylic acids and/or derivatives thereof include benzoic acid, propionic acid, butyric acid, oxalic acid, succinic acid, lactic acid, acetic acid, formic acid, citric acid, acrylic acid, malonic acid, maleic acid, malic acid, valeric acid, acetoacetic acid, butyramide, succinimide, succinamide, and succinamic acid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG.1 is a diagram showing the relationship of heating temperatures for chromate treatment, the amount of Cr^{6+} (%) and the value of b when 1% of a carboxylic acid is added and when not added.

FIG.2 is a diagram illustrating the relationship of heating temperatures for chromate treatment and corrosion resistance when 1% of a carboxylic acid is added and when not added.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in further detail.

Chromic acid and/or products prepared through the reduction of chromic acid will be first described. A solution containing chromic anhydride as a main component is generally used to achieve corrosion resistance and form a uniform coating on at least one surface of a steel material through chromate treatment. To achieve an aesthetic appearance, it is necessary to reduce this chromic acid and achieve a certain proportion of Cr^{3+}. Therefore, the proportion of Cr^{3+} should range from 1/2 to 1/1 of the total weight of Cr^{6+}.

Namely, when the proportion of Cr^{3+} to Cr^{6+} is less than 1/2 by weight, it is difficult to reduce the amount of Cr^{6+} on the surface of the steel material after dried to 20% or less of the total amount of chromium (hereinafter referred to as "T-Cr"). Therefore, an aesthetic appearance of the steel material, particularly the suppression of its yellow tint, cannot be achieved.

Moreover, Cr^{3+} is too large in quantity and in the proportion of more than 1/1 to Cr^{6+}, precipitates are easily generated in the solution, thus making it difficult to preserve the solution and form a coating.

The content of chromic acid and/or reduced products of chromic acid in the solution should be 1 to 15% by weight of the solution. When it is less than 1%, it is difficult to achieve the satisfactory amount of chromium adhered, and when it is more than 15%, the solution may be unstable.

Colloidal silica will be described in the following.

It is already known that corrosion resistance can be enhanced and a non-uniform chromate coating can be prevented by adding silica in the solution. However, only this cannot meet the needs of current users for an aesthetic appearance of the surface of steel materials. According to research conducted by the present inventors, when a steel strip to which a silica-added chromate solution is applied is dried at a temperature of less than 150°C, an aesthetic appearance is rarely achieved. However, Cr^{6+} on the surface of the steel material can be reduced by baking the strip at a high temperature of 220°C or more, preferably 240°C or more, and a strong chromate film can be formed through dehyration and condensation reactions with silica, whereby a yellow tint caused by Cr^{6+} can be eliminated and the appearance of the material can be improved. It is also discovered that corrosion resistance is further enhanced by drying at high temperatures as described above.

Such effects of adding silica cannot be achieved when the amount of silica added, calculated as SiO_2, is less than 1/2 of the total amount of chromium. However, when it is more than 6, ill effects such as increased surface resistance of the steel material are produced. Therefore, the proportion of silica added is limited to 1/2 to 6 of the weight of T-Cr.

Carboxylic acids and derivatives thereof will be described in the following.

Carboxylic acids and derivatives thereof are stable in the chromate solution at normal temperatures, but they are decomposed and changed into lower molecular hydrocarbons when dried at high temperatures. In this process, they reduce Cr^{6+} to Cr^{3+}. Remaining hydrocarbons are included in a chromate film, resulting in the thicker chromate film. Therefore, to improve the appearance by eliminating the yellow tint caused by Cr^{6+} and achieve corrosion resistance by increasing the thickness of the chromate film, 0.1% or more by weight of carboxylic acids and/or derivatives thereof must be added. However, when more than 10% by weight of carboxylic acids and/or derivatives thereof is added, it will result in non-uniform drying. Therefore, addition is limited to 0.1 to 10% by weight.

Resin chromate treatment wherein polycarboxylic acids such as polyacrylic acids and esters thereof, and derivatives thereof are added to a chromate solution for chromate treatment is known as a prior art. Carboxylic acids and/or derivatives thereof used in the present patent application are not used to form a resin film through copolymerization as above-described, but are oxidated and decomposed through the reduction of Cr^{6+} to Cr^{3+}. Consequently, the present invention is totally and technically different from the prior art.

Preferable carboxylic acids and/or derivatives thereof having above described function include benzoic acid, propionic acid, butyric acid, oxalic acid, succinic acid, lactic acid, acetic acid, formic acid, citric acid, acrylic acid, malonic acid, maleic acid, malic acid, valeric acid, acetoacetic acid, butyramide, succinimide, succinamide, and succinamic acid.

The baking temperature should be 150 ° C or more, preferably 200 ° C or more, to eliminate a yellow tint caused by Cr^{6+} and to form a strong chromate film in order to achieve corrosion resistance as described in the foregoing. However, when it is higher than 300 ° C, production cost becomes high and accordingly, the baking temperature is limited to the range of 150 ° C to 300 ° C.

Such baking is accompanied by the reduction reaction of Cr^{6+} in the chromate solution adhered to the surface of the steel material to Cr^{3+}, and therefore is an extremely important process which is substantially different in function from the drying process which is aimed only at evaporating water. The proportion of Cr^{6+} in the chromate film can be reduced to 20% or less of the weight of T-Cr through this process, thus making it possible to produce a chromate-treated steel material having an aesthetic appearance and excellent chromium elution resistance.

The amount of chromium deposited should be in the range of 10 to 150 mg/m^2. If the amount is less than the lower limit, corrosion resistance is not satisfactory, and if the amount is more than the upper limit, a good appearance cannot be attained.

Steel materials to which the present invention is applied are not limited by plating means such as hot dipping, electroplating and vapor depositting, and may be plated with zinc or zinc alloys including two-element alloys such as Zn-Ni, Zn-Fe and Zn-Al, or multi-element alloys such as Zn-Ni-Co and Zn-Al-Cr. The present invention can be applied to strip, angled member, pipe and steel wire, and not limited by kind of steel material.

EXAMPLES

The present invention will be explained with reference to examples given below. However, the present invention is not limited by these examples.

Example 1

To clarify the effects of the present invention, a basic chromate solution is prepared by mixing chromic anhydride, distilled water, ethylene glycol and colloidal silica (Snowtex 0 manufactured by Nissan Chemical K.K.), and various carboxylic acids and/or derivatives thereof are further added to the solution to prepare chromate solutions having compositions shown in Table 1 and Table 2. The solutions are applied by use of a bar coater to a pure zinc electroplated steel sheet having a zinc deposit weight of 20 g/m^2, a zinc hot dipped steel sheet having a zinc deposit weight of 60 g/m^2, and a 5% Al-zinc alloy plated steel sheet (dimention of all the sheets being 1 x 100 x 200 mm). The corrosion resistance, appearance and chromium elution of each steel sheet are evaluated by changing the heating temperature from 50 ° C to 300 ° C in terms of sheet temperature. The results are shown in Table 3.

A salt spray test was carried out according to JIS Z 2371 to test corrosion resistance in terms of white rust generation rate for a zinc plated steel sheet during the period of 240 hours. The appearance of the sheet is evaluated by the presence or absence of a non-uniform coating through visual inspection. The yellow tint is judged by measuring the values of L, a and b according to JIS Z 8729 using an SM color computer (manufactured by Suga Test Instrument Co., Ltd.). The value of b is used.

The amount of eluted chromium is detected by immersing the sheet in an alkali degreasing solution (CL364S 2% solution manufactured by Japan Parkerizing Co., Ltd., 60 ° C) for two minutes and measuring the amount of chromium deposited before and after the immersion using a fluorescent X ray analysis. The amount of eluted chromium is expressed in percentage.

The quantitative analysis of Cr^{3+} and Cr^{6+} on the surface of the steel sheet was carried out by means of ESCA.

The amount of chromium deposited is measured by a fluorescent X ray and expressed in mg/m^2.

FIG.1 and FIG.2 are graphs showing the relationship of heating temperature, corrosion resistance, the value of b and Cr^{6+} (%) on the surface when the heating temperature was changed after chromate treatment was carried out using the same steel sheet and chromate solution as those of the present invention as shown in No.1 of Table 1. At this time, the amount of chromium deposited was approximately 45 mg/m^2.

According to FIG.1, the amount of hexavalent chromium begins to decrease when the temperature goes beyond 200 ° C, and more than 10% of hexavalent chromium remains even at 300 ° when no carboxylic acid is added. In contrast, the amount of hexavalent chromium decreases at 150 ° C or more, and becomes null at 220 ° C or more, and the value of b is 0 or less when a carboxylic acid is added according to the present invention. The effects of the present invention are thus understood.

FIG.2 shows the results of corrosion resistance tests. When no carboxylic acid is added, a drying temperature of 200 ° C or more is required to achieve satisfactory corrosion resistance. However, when a carboxylic acid is added, satisfactory corrosion resistance can be achieved at a temperature of 150 ° C or more.

Furthermore, according to the results shown in Tables 1, 2 and 3, all of the steel sheets produced by the method of the present invention have an aesthetic uniform appearance (no irregularities observed and a b value of 3.5 or less), corrosion resistance (240 hours of salt spray, white rust generation rate of 5% or less), and a slight amount of eluted chromium (5% or less). In contrast, steel strips dried at a temperature of less than 150 ° C have a b value of more than 3.5, and is inferior to the former steel sheets in chromium elution (10% or more) and corrosion resistance (5% or more) (refer to Sample Nos. 33 and 38).

When the ratio of Cr^{3+} to Cr^{6+} is less than 1/2, the concentration of Cr^{6+} on the surface of the steel sheet after dried is high, and the value of b is more than 3.5 resulting in a poor appearance (refer to Sample No.25).

On the contrary, when the ratio of Cr^{3+} to Cr^{6+} is more than 1, the chromate solution becomes unstable with the result that a non-uniform coating is easily produced (refer to Sample No.34).

When the amount of silica added is too small, satisfactory corrosion resistance cannot be achieved (refer to Sample No.27), while when the amount of silica added is too large, a non-uniform coating is easily produced (refer to Sample No.26).

When the amount of a carboxylic acid added is too small, the concentration of Cr^{6+} on the surface of the steel material becomes high whereby an aesthetic uniform appearance (a b value of 3.5 or less) and chromium elution resistance (5% or less) cannot be achieved (refer to Sample No.21). When the amount is too large, a non-uniform coating is easily produced (refer to Sample No.22).

When the zinc coating weight is too small, satisfactory corrosion resistance cannot be achieved (refer to Sample No.28), while when the weight is too large, the b value is more than 3.5, and an aesthetic appearance cannot be achieved (refer to Sample No.29).

As described in the foregoing, a chromate-treated plate steel material having corrosion resistance and an aesthetic uniform appearance can be produced by the method of the present invention.

Table 1-1

No.	kind of steel sheet	chromate solution composition				remarks
		T-Cr (% by weight)	Cr^{3+}/Cr^{6+} (weight ratio)	SiO_2/T-Cr (weight ratio)	carboxylic acid (% by weight)	
1	pure zinc electroplated steel sheet	4	0.80	3.0	–	Comparative example
2	pure zinc electroplated steel sheet	4	0.80	3.0	benzoic acid (0.5%)	Example
3	pure zinc electroplated steel sheet	4	0.80	3.0	propionic acid (0.5%)	Example
4	pure zinc electroplated steel sheet	4	0.80	3.0	butyric acid (0.5%)	Example
5	pure zinc electroplated steel sheet	4	0.80	3.0	oxalic acid (0.5%)	Example
6	pure zinc electroplated steel sheet	4	0.80	3.0	succinic acid (0.5%)	Example
7	pure zinc electroplated steel sheet	4	0.80	3.0	lactic acid (0.5%)	Example
8	pure zinc electroplated steel sheet	4	0.80	3.0	acetic acid (0.5%)	Example
9	pure zinc electroplated steel sheet	4	0.80	3.0	formic acid (0.5%)	Example
10	pure zinc electroplated steel sheet	4	0.80	3.0	citric acid (0.5%)	Example
11	pure zinc electroplated steel sheet	4	0.80	3.0	acrylic acid (0.5%)	Example
12	pure zinc electroplated steel sheet	4	0.80	3.0	malonic acid (0.5%)	Example

* The underlined represents conditions outside the scope of the present invention.

Table 1-2

No.	kind of steel sheet	chromate solution composition				remarks
		T-Cr (% by weight)	Cr^{3+}/Cr^{6+} (weight ratio)	SiO_2/T-Cr (weight ratio)	carboxylic acid (% by weight)	
13	pure zinc electroplated steel sheet	4	0.80	3.0	maleic acid (0.5%)	Example
14	pure zinc electroplated steel sheet	4	0.80	3.0	malic acid (0.5%)	Example
15	pure zinc electroplated steel sheet	4	0.80	3.0	valeric acid (0.5%)	Example
16	pure zinc electroplated steel sheet	4	0.80	3.0	acetoacetic acid (0.5%)	Example
17	pure zinc electroplated steel sheet	4	0.80	3.0	butyramide (0.5%)	Example
18	pure zinc electroplated steel sheet	4	0.80	3.0	succinimide (0.5%)	Example
19	pure zinc electroplated steel sheet	4	0.80	3.0	succinamide (0.5%)	Example
20	pure zinc electroplated steel sheet	4	0.80	3.0	succinamic acid (0.5%)	Example
21	pure zinc electroplated steel sheet	4	0.80	3.0	lactic acid (0.08%)	Comparative example
22	pure zinc electroplated steel sheet	4	0.80	3.0	succinic acid (12%)	Comparative example
23	pure zinc electroplated steel sheet	4	0.80	3.0	citric acid (0.5%) succinic acid (0.5%)	Example
24	pure zinc electroplated steel sheet	4	0.80	3.0	lactic acid (0.5%) citric acid (0.5%) succinic acid (0.5%)	Example

* The underlined represents conditions outside the scope of the present invention.

Table 2

No.	kind of steel sheet	chromate solution composition				remarks
		T-Cr (% by weight)	Cr^{3+}/Cr^{6+} (weight ratio)	SiO_2/T-Cr (weight ratio)	carboxylic acid (% by weight)	
25	pure zinc electroplated steel sheet	4	0.40	3.0	oxalic acid (0.5%)	Comparative example
26	pure zinc electroplated steel sheet	4	0.80	7.3	succinic acid (0.5%)	Comparative example
27	pure zinc electroplated steel sheet	4	0.80	0.40	lactic acid (0.5%)	Comparative example
28	pure zinc electroplated steel sheet	4	0.85	3.0	acetic acid (0.5%)	Comparative example
29	pure zinc electroplated steel sheet	4	0.85	3.0	acetic acid (0.5%)	Comparative example
30	zinc hot dipped steel sheet	3	0.80	4.0	acetic acid (0.5%) acrylic acid (0.5%)	Example
31	zinc hot dipped steel sheet	3	0.80	4.0	malic acid (0.5%) citric acid (0.5%)	Example
32	zinc hot dipped steel sheet	3	0.80	4.0	succinic acid (0.5%) succinimide (0.5%) acetic acid (0.5%)	Example
33	zinc hot dipped steel sheet	3	0.80	4.0	succinic acid (0.5%) succinimide (0.5%) acetic acid (0.5%)	Comparative example
34	zinc hot dipped steel sheet	3	1.20	4.0	succinic acid (0.5%) succinimide (0.5%) acetic acid (0.5%)	Comparative example
35	5% Al-Zn alloy plated steel sheet	2.5	0.60	2.0	butyric acid (0.5%) oxalic acid (0.5%)	Example
36	5% Al-Zn alloy plated steel sheet	2.5	0.60	2.0	malonic acid (0.5%) citric acid (0.5%)	Example
37	5% Al-Zn alloy plated steel sheet	2.5	0.60	2.0	acrylic acid (0.5%) malic acid (0.5%)	Example
38	5% Al-Zn alloy plated steel sheet	2.5	0.60	2.0	acrylic acid (0.5%) malic acid (0.5%)	Comparative example

* The underlined represents conditions outside the scope of the present invention.

Table 3-1

No.	amount of deposited chromium (mg/m^2)	drying temperature (°C)	Cr^{6+} on surface (Cr^{6+}/T-Cr) (% by weight)	evaluation results				remarks
				appearance	b value	corrosion resistance (white rust generation rate in %)	amount of eluted chromium (%)	
1	45	200	<u>32</u>	good	4.2	4	18	Comparative example
2	48	200	8	good	1.8	1	4	Example
3	46	200	6	good	1.5	1	3	Example
4	42	180	15	good	2.2	2	7	Example
5	38	180	14	good	2.0	2	7	Example
6	35	160	18	good	2.1	3	8	Example
7	46	220	5	good	0.5	0	2	Example
8	48	220	5	good	0	0	2	Example
9	52	240	2	good	-0.3	0	1	Example
10	55	240	2	good	-0.5	0	1	Example
11	58	260	less than 1%	good	-0.8	0	less than 1%	Example
12	60	260	less than 1%	good	0.5	0	less than 1%	Example
13	82	280	less than 1%	good	0.7	0	less than 1%	Example
14	80	280	less than 1%	good	0.7	0	less than 1%	Example
15	90	300	less than 1%	good	1.1	0	less than 1%	Example
16	49	250	less than 1%	good	-0.8	0	less than 1%	Example
17	52	250	less than 1%	good	-0.4	0	less than 1%	Example
18	54	250	less than 1%	good	-1.0	0	less than 1%	Example
18	95	300	less than 1%	good	1.2	0	less than 1%	Example
20	110	300	less than 1%	good	1.9	0	less than 1%	Example

* The underlined represents conditions other than the scope of the present invention.

Table 3-2

No.	amount of deposited chromium (mg/m^2)	drying temperature (°C)	Cr^{6+} on surface (Cr^{6+}/T-Cr) (% by weight)	evaluation results				remarks
				appearance	b value	corrosion resistance (white rust generation rate in %)	amount of eluted chromium (%)	
21	48	250	less than 1%	irregularities observed	-1.5	2	less than 1%	Comparative example
22	50	250	33	good	4.6	0	14	Comparative example
23	87	230	less than 1%	good	2.3	0	less than 1%	Example
24	128	240	less than 1%	good	2.4	0	less than 1%	Example
25	56	200	37	good	4.5	0	21	Comparative example
26	52	250	less than 1%	irregularities observed	-0.8	0	less than 1%	Comparative example
27	48	250	less than 1%	good	-1.0	25	less than 1%	Comparative example
28	8	250	less than 1%	good	-1.3	78	less than 1%	Comparative example
29	162	250	less than 1%	good	4.3	0	less than 1%	Comparative example
30	35	260	less than 1%	good	-0.5	0	less than 1%	Example
31	32	260	less than 1%	good	0.1	0	less than 1%	Example
32	37	260	less than 1%	good	-0.3	0	less than 1%	Example
33	34	130	35	good	4.6	12	18	Comparative example
34	31	240	less than 1%	irregularities observed	-0.6	0	less than 1%	Comparative example
35	22	230	less than 1%	good	-0.4	0	less than 1%	Example
36	21	230	less than 1%	good	-0.2	0	less than 1%	Example
37	18	230	less than 1%	good	-0.7	0	less than 1%	Example
38	24	100	33	good	3.8	8	14	Comparative example

* The underlined represents conditions other than the scope of the present invention.

As described in the foregoing, according to the present invention, it is possible to produce a chromate-treated plated steel strip which achieves an improved appearance thereof, particularly the minimization of a yellow tint peculiar to chromate, and enhanced corrosion resistance simultaneously and at a lower cost, which has been difficult with a prior art.

Claims

1. A method for producing a chromate-treated plated steel material, comprising the steps of

   applying on at least one surface of a zinc- or zinc alloy-plated steel material a solution containing 1 to 15% by weight of chromic acid and/or reduced products of chromic acid having trivalent chromium and hexavalent chromium in the proportion of 1/2 to 1/1 by weight as the total amount of metal chromium, colloidal silica, calculated as SiO_2, in the proportion of 1/2 to 6/1 of the total weight of chromium, and further 0.1 to 10% by weight of at least one selected from the group consisting of carboxylic acids and/or derivatives thereof, which are stable in said solution,

   heating and baking said chromate-treated steel material at a temperature ranging from 150 ° C to 300 ° C to form a chromate film having hexavalent chromium on the surface thereof in the proportion of 20% or less of the total weight of chromium and having a deposit of 10 to 150 mg/m^2 calculated as chromium.

2. A method for producing a chromate-treated plated steel material according to claim 1, wherein carboxylic acids and/or derivatives thereof include benzoic acid, propicnic acid, butyric acid, oxalic acid, succinic acid, lactic acid, acetic acid, formic acid, citric acid, acrylic acid, malonic acid, maleic acid, malic acid, valeric acid, acetoacetic acid, butyramid, succinimide, succinamide, and succinamic acid.

Fig.1

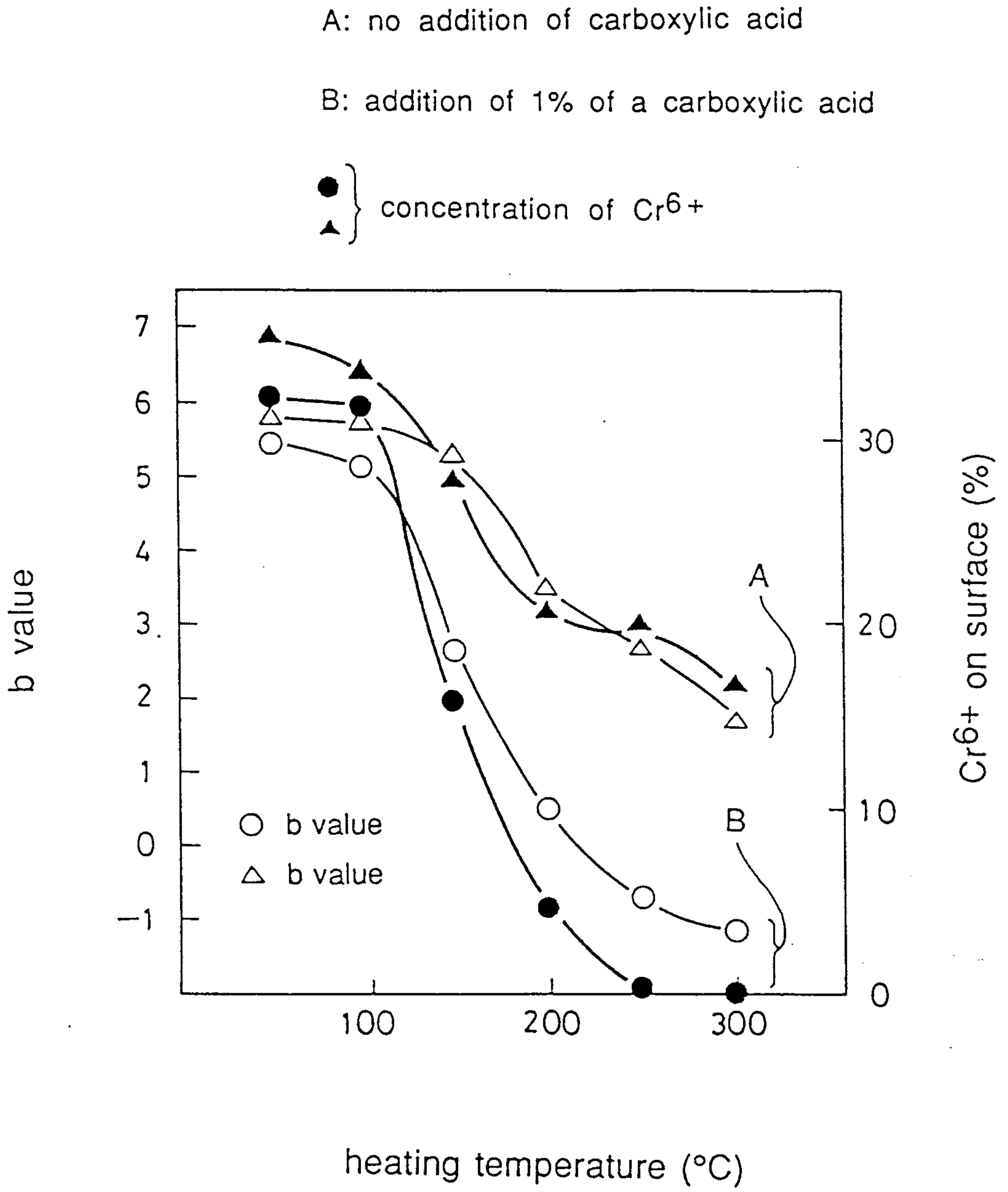
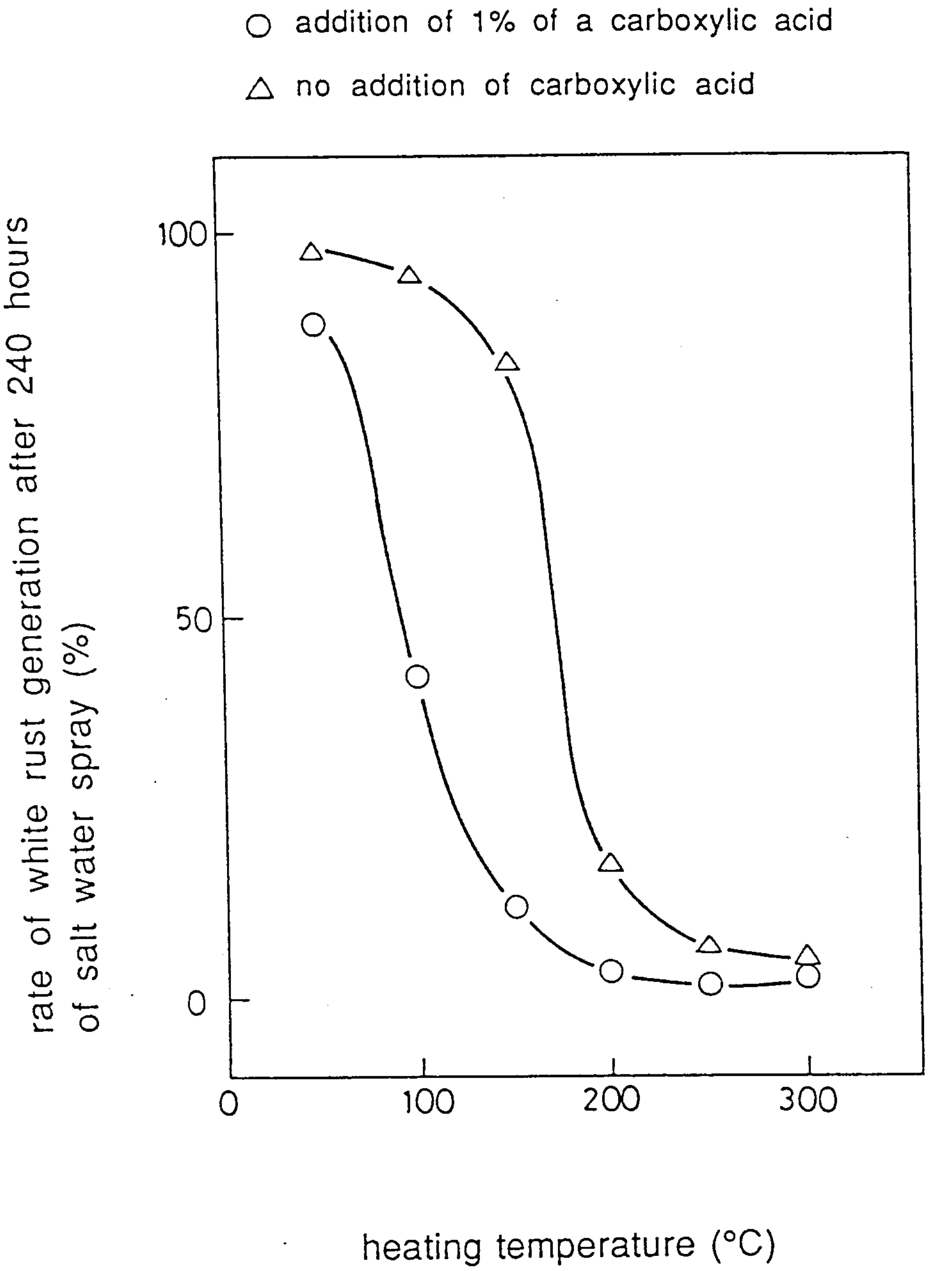

A: no addition of carboxylic acid
B: addition of 1% of a carboxylic acid
● ▲ } concentration of Cr^{6+}
○ b value
△ b value
A
B
b value
7
6
5
4
3
2
1
0
−1
Cr^{6+} on surface (%)
30
20
10
0
100
200
300
heating temperature (°C)

Fig.2


○ addition of 1% of a carboxylic acid
△ no addition of carboxylic acid
rate of white rust generation after 240 hours of salt water spray (%)
100
50
0
0
100
200
300
heating temperature (°C)

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 12 2028

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	EP-A-0 308 563 (SUMITOMO METAL INDUSTRIES LTD) * claims 1,3,10; example 1; table 1 * ---	1,2
X	PATENT ABSTRACTS OF JAPAN vol. 8, no. 11 (C-205)(1448) 18 January 1984 & JP-A-58 177 475 (NITSUSHIN SEIKOU KK) 18 October 1983 * abstract * ---	1,2
Y	FR-A-2 203 862 (DIAMOND SHAMROCK CORPORATION) * claims 1,5,6,13,15 * ---	1,2
Y	FR-A-2 550 551 (NIPPON LIGHT METAL COMPANY LIMITED) * claims 1,2; example 1; table 3 * ---	1,2
A	US-A-3 720 549 (ROBERT G. HIRST) ---	
A	BE-A-667 113 (SOCIETE CONTINENTALE PARKER) -----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.5)

C23C22/74

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 APRIL 1992	LANDAIS A.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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