

DESCRIPTION

PASSIVATION TREATMENT SOLUTION FOR TINPLATE, TINPLATE AND MANUFACTURING METHOD THEREFOR

TECHNICAL FIELD

The present invention relates to a surface treatment solution and a process, particularly to a surface treatment solution for tinplate and a process.

BACKGROUND

In order to endow metal cans with a beautiful appearance and good corrosion resistance, tinplate generally needs to be surface coated before being formed into metal cans, i.e., coated with one or more layers of organic coating on the surface of the tinplate and cured into a film, so that the metal can is endowed with a beautiful appearance and good corrosion resistance. Thus, decorative coating performance is a critical application performance index of tinplates.

In order to endow tinplate with good decorative coating performance, it is necessary to perform passivation on the surface tin layer of the tinplate to prevent rapid oxidation of tin and to improve decorative coating performance.

The conventional surface treatment technique for tinplate involves chromate electrolytic passivation, i.e., placing the tinplate in a chromate solution and performing cathodic electrolytic treatment to form a passivation film layer containing chromium oxides on the surface of the tinplate. The chromate used in this process is typically dichromate or chromic anhydride. However, long-term usage has shown that this simple chromium oxide passivation film cannot provide tinplate with fully satisfactory decorative coating performance. Defects such as poor lacquer wettability and poor adhesion of the lacquer film often occur, affecting the normal use of the tinplates.

In addition, the US patent document with publication number US3925171A mentions a method of depositing metallic chromium and chromium oxide on the surface of tinplate, which can improve the adhesion of the lacquer film of tinplate.

In view of the above, the present invention aims to provide a passivation treatment solution for tinplate, which can improve the decorative coating performance of tinplate by performing a passivation treatment on the tinplate using the passivation treatment solution.

SUMMARY

One of the objectives of the present invention is to provide a passivation treatment solution for tinplate, which can endow the surface of the tinplate with better lacquer wettability and better adhesion of lacquer film, improving and solving the decorative coating problems encountered by conventional tinplates.

In order to achieve the above objective, the present invention provides a passivation treatment solution for tinplate, which comprises the following active ingredients:

chromic anhydride, which has a content of 15-30 g/l;

metaphosphoric acid and/or metaphosphate, which has a content of 5-15 g/l;

ammonium bromide, which has a content of 1-5 g/l;

nitrogen-containing organic compound, which has a content of 0.2-2 g/l.

In the passivation treatment solution of the present invention, chromic anhydride is the source of chromium in the tinplate surface passivation film, metaphosphoric acid and its salt are the source of phosphorus in the passivation film, and ammonium bromide and nitrogen-containing organic compound increases the dispersion ability and current efficiency of the passivation solution. The addition of phosphorus can increase the adhesion between the tinplate and the lacquer film.

Preferably, the content of chromic anhydride may be 18-28 g/L, or 20-25 g/L, such as 22 g/L; the content of metaphosphoric acid and/or metaphosphate may be 6-13 g/L, or 8-11 g/L, such as 9 g/L, 10 g/L; the content of ammonium bromide may be 2-4.5 g/L, or 2.5-4 g/L, or 3-4 g/L, such as 3.5g /L; the content of nitrogen-containing organic compounds may be 0.5-1.8 g/L, 0.8-1.5 g/L, or 1-1.2 g/L.

Preferably, in the passivation treatment solution of the present invention, the nitrogen-containing organic compound comprises at least one of thiourea, glycine and niacin.

Preferably, in the passivation treatment solution of the present invention, the metaphosphate is an inorganic salt of metaphosphoric acid, such as potassium salt of metaphosphoric acid, sodium salt of metaphosphoric acid, etc.

Preferably, in the passivation treatment solution of the present invention, in addition to chromic anhydride, chromic acid and its salts, such as chromic acid, potassium chromate and sodium chromate, can also be used as the source of chromium.

Preferably, the passivation treatment solution according to the present invention has a pH value of 1.2-3.8. This pH range can be adjusted by using phosphoric acid and sodium hydroxide. The pH value may also be 1.5-3.5, or 2-3.2, or 2.5-3.

Another objective of the present invention is to provide a tinplate with excellent decorative coating performance. The surface of the tinplate has excellent coating wettability and better adhesion of lacquer film, thereby improving and solving the coating problems encountered by conventional tinplate.

In view of this, the present invention also provides a tinplate with excellent decorative coating performance, comprising a steel substrate and a metallic tin layer on the steel substrate, wherein the metallic tin layer has a surface passivation film formed by the passivation treatment solution as described above on its surface.

Preferably, the tinplate of the present invention has a surface passivation film that comprises metallic chromium, a trivalent chromium oxide, a tin oxide and phosphorus, and that does not contain hexavalent chromium.

Preferably, in the surface passivation film of the present invention, the content of metallic chromium is 0.5-2.5 mg/m², which can also be 0.8-2.2 mg/m², 1.1-2 mg/m², or 1.2-1.8 mg/m²; the content of trivalent chromium oxide is 2-7 mg/m², which can also be 2.5-6.3 mg/m², 3.1-5.6 mg/m², or 3.7-4.8 mg/m², such as 4.5 mg/m²; the content of phosphorus is 0.3-5 mg/m², which can also be 0.6-4.1 mg/m², 1.2-3 mg/m², or 1.7-2.4 mg/m², such as 1.9 mg/m²; the content of tin oxide is 0.5-2 mC/cm², which can also be 0.9-1.9 mC/cm², 1.1-1.8 mC/cm², 1.3-1.7 mC/cm², or 1.4-1.5 mC/cm².

It should be noted that, in this technical field, the content of tin oxide is commonly expressed in millicoulombs per square centimeter (mC/cm²), which specific refers to the amount

of reduction charge required for tin oxide to completely remove oxide film by cathodic electrolysis in a low concentration (e.g. 0.001 mol/L) hydrogen bromide solution.

Preferably, the tinplate of the present invention has a lacquer film adhesion level of Grade 1.

Preferably, the tinplate of the present invention has a surface water contact angle of $\leq 76^\circ$.

Another objective of the present invention is to provide a method for manufacturing the tinplate with excellent coating performance. The tinplate produced by this method has a surface with excellent coating wettability and better adhesion of lacquer film.

In view of this, the present invention also provides a method for manufacturing tinplate, including the following steps: a) performing a pretreatment on a tinplate substrate after reflowing to remove tin oxide film on the surface of the tinplate substrate; b) performing a passivation on the pretreated tinplate substrate, wherein the passivation step includes immersing the pretreated tinplate substrate in the above-mentioned passivation treatment solution, and subjecting the tinplate substrate to cathodic electrolytic treatment as a cathode.

Preferably, in the method of the present invention, the pretreatment includes immersing the tinplate substrate after reflowing in a chromic anhydride solution, wherein the chromic anhydride solution has a chromic anhydride content of 10-20g/L.

The tinplate substrate of the present invention can be prepared using conventional methods commonly known in the art. Preferably, it is prepared using a method including the following steps in sequence: alkali washing (degreasing), pickling (activating the surface), electroplating tin on steel substrate to form a metallic tin layer thereon, and reflowing (alloying) the tinplate substrate.

Preferably, the method of the present invention further includes cleaning the surface of the tinplate with clean water after the passivation step until there is no residual chromate.

Since the amount of tin plating on a single side of the tinplate ranges from 0.3-15 g/m², it is usually necessary to perform reflow alloying treatment on the tinplate substrate. This involves rapidly heating the tinplate substrate to a specific temperature above the melting point of metallic tin (e.g., 240-310 °C), thereby forming a tin-iron alloy layer between the steel substrate and the metallic tin layer. As tin is susceptible to oxidation, this process can generate a significant amount of tin oxides on the surface of the tinplate.

In the present invention, by the step of immersing the tinplate substrate after tin plating and reflowing in a chromic anhydride solution for pretreatment, the tin oxide film on the surface can be removed prior to passivation, thereby controlling the content of tin oxide in the finished product.

Preferably, in the method of the present invention, the pretreatment is performed for a period of 2-10 s.

Preferably, in the method of the present invention, the chromic anhydride solution has a temperature of 30-50 °C.

Preferably, in the method of the present invention, the passivation treatment solution has a temperature of 40-65 °C.

Preferably, in the method of the present invention, the cathodic electrolytic treatment has a cathodic current density of 15-60 C/dm².

Preferably, the method of the present invention further includes the steps of squeeze-drying the passivated and cleaned tinplate with a squeeze roller, followed by drying the surface of the tinplate with hot air at a temperature not lower than 80 °C; coating the dried tinplate with conventional DOS oil (dioctyl sebacate) to obtain the finished product.

Compared with prior arts, the passivation treatment solution, the resulting tinplate and the manufacturing method therefor described in the present invention have the following beneficial effects:

The passivation treatment solution of the present invention uses a relatively low concentration of chromic anhydride and is free of fluorine, reducing the corrosion to production equipment, reducing the environmental load and the environmental treatment cost of chromate wastewater.

The tinplate obtained by using the passivation treatment solution and manufacturing method of the present invention has excellent coating performance, which is more conducive to the full spreading and wetting of the coating on the tinplate surface, and the formation of a strong adhesion between the cured lacquer film and the tinplate. This significantly reduces the quality hazards of coating dewetting and poor adhesion of the lacquer film, and is more conducive to control the amount of tin oxides on the surface of the tinplate at a lower level, enhancing its

resistance to aging and maintaining good coating performance. Even after long-term storage, the coating performance does not deteriorate.

DETAILED DESCRIPTION

The passivation treatment solution, tinplate and manufacturing method therefor according to the present invention will be further explained and illustrated with specific embodiments. However, the explanations and illustrations do not constitute undue limitations on the technical solutions of the present invention.

Examples 1-9 and Comparative Examples 1-3

The tinplates of Examples 1-9 of the present invention were manufactured by the following steps:

- (1) alkali washing the steel substrate;
- (2) pickling;
- (3) electroplating tin on the steel substrate to form a metallic tin layer, wherein the amount of tin plating was 2.8 g/m^2 ;
- (4) reflowing tinplate substrate;
- (5) pretreatment: immersing the tinplate substrate after reflowing into a chromic anhydride solution, wherein the chromic anhydride content in the chromic anhydride solution was 10-20g/L, and the temperature of the chromic anhydride solution was 30-50 °C, and pretreatment duration was 2-10 s;
- (6) passivation: immersing the pretreated tinplate substrate into a passivation treatment solution as listed in Table 2, adjusting the pH of the passivation treatment solution to 1.2-3.8 with phosphoric acid and sodium hydroxide, and the temperature of the passivation treatment solution was 40-65 °C. The tinplate was used as the cathode in a cathodic electrolytic treatment, with a cathodic current density of $15\text{-}60 \text{ C/dm}^2$. After passivation treatment, the surface of the tinplate was rinsed with clean water until there was no residual chromate. After squeeze-drying the passivated and cleaned tinplate by using a squeeze roller, the tinplate surface was dried with hot air at a temperature not lower than 80 °C;
- (7) applying DOS oil.

It should be noted that, in order to demonstrate the implementation effect of the present invention, in Comparative Examples 1-3, the pretreatment step was not carried out, and the passivation treatment step was carried out by using a conventional process, wherein the passivation solution was a sodium dichromate solution of 25 g/L, and the passivation treatment solution of the present invention was not used.

Table 1 lists the specific process parameters of the pretreatment process in Examples 1-9.

Table 1.

	Chromic anhydride content in chromic anhydride solution (g/L)	Temperature of chromic anhydride solution (°C)	Pretreatment duration (s)
Example 1	12	30	4
Example 2	10	35	8
Example 3	18	45	2
Example 4	15	45	3
Example 5	15	40	9
Example 6	12	50	5
Example 7	20	40	2
Example 8	10	45	10
Example 9	16	35	7

Table 2 lists the composition of the passivation treatment solution of Examples 1-9 of the present invention and Comparative Examples 1-3.

Table 2.

	Content of sodium dichromate (g/L)	Content of chromic anhydride (g/L)	Content of metaphosphoric acid and/or metaphosphate (g/L)	Kinds of metaphosphoric acid and/or metaphosphate	Ammonium bromide (g/L)	Kinds of nitrogen - containing organic compound	Content of nitrogen - containing organic compound (g/L)
Example 1	-	20	10	metaphosphoric acid + sodium hexametaphosphate	4.5	thiourea + glycine + niacin	1
Example 2	-	30	5	metaphosphoric acid	1	thiourea	2
Example 3	-	15	15	metaphosphoric acid + sodium hexametaphosphate	2	niacin + glycine	1.2
Example 4	-	25	8	metaphosphoric acid	3	niacin	1.8
Example 5	-	22	11	metaphosphoric acid + potassium metaphosphate	5	thiourea + niacin	0.2
Example 6	-	28	10	metaphosphoric acid + potassium metaphosphate	4	niacin + glycine	1
Example 7	-	18	9	phosphoric acid + sodium hexametaphosphate	3	glycine	0.5
Example 8	-	15	13	phosphoric acid + potassium polymetaphosphate	2.5	thiourea + glycine	1.5
Example 9	-	20	6	potassium polymetaphosphate	3.5	niacin	0.8
Comparative Example 1	25	-	-	-	-	-	-
Comparative Example 2	25	-	=	-	-	-	-
Comparative Example 3	25	-	=	-	-	-	-

Table 3 lists the process parameters of the passivation step for Examples 1-9 of the present invention and Comparative Examples 1-3.

Table 3.

	pH of passivation treatment solution	Temperature of passivation treatment solution (°C)	Cathodic current density (C/dm ²)
Example 1	3.2	65	40
Example 2	1.2	45	55
Example 3	3.8	55	25
Example 4	1.5	40	60
Example 5	2	50	45
Example 6	3	65	15
Example 7	2	55	35
Example 8	3.5	60	30
Example 9	2.5	40	50
Comparative Example 1	<u>4.5</u>	45	20
Comparative Example 2	<u>4.5</u>	45	40
Comparative Example 3	<u>4.5</u>	45	60

To verify the implementation effect of the present invention, the inventors tested the composition of the surface passivation film in Examples 1-9 and Comparative Examples 1-3, and the results are listed in Table 4.

In addition, coating performance evaluation tests were conducted on Examples 1-9 and Comparative Examples 1-3, including:

(1) Surface Wettability Test

The surface wettability of the tinplates of the examples and comparative examples were measured by using a contact angle tester, and the test medium was water. The surface wettability of each example and comparative example are listed in Table 4.

(2) Adhesion of Lacquer Film Performance

The evaluation method of lacquer film adhesion performance refers to the adhesion of lacquer film evaluation method adopted in QB/T 2763-2006 "Coated Tin (or Chromium)-plated Thin Steel Plates". The coating was a certain type of commercially available epoxy phenolic coating, and was applied to the surface of the tinplate involved in the examples and comparative examples. The dry film weight of the lacquer film was 10 g/m². The adhesion performance of the

coating film was evaluated based on the percentage of the peeling area of the lacquer film. The adhesion performance of the lacquer film of the tinplate of each example and comparative example are listed in Table 4.

Table 4.

	Composition of surface passivation film				Coating performance evaluation	
	SnOx (mC/cm ²)	Cr (mg/m ²)	Cr ₂ O ₃ (mg/m ²)	P (mg/m ²)	Contact angle (°)	Adhesion of lacquer film (Grade)
Example 1	1.9	1.2	2	0.3	75.4	1
Example 2	1.8	2.5	4.8	2.4	74.6	1
Example 3	1.3	0.8	7	1.7	68.3	1
Example 4	0.9	2.2	3.1	3	71	1
Example 5	1.7	1.8	4.5	4.1	72.3	1
Example 6	1.4	0.5	2.5	0.6	69.9	1
Example 7	1.1	1.1	3.7	1.2	67.3	1
Example 8	1.5	1.2	6.3	5	70.7	1
Example 9	0.5	2	5.6	1.9	66.5	1
Comparative Example 1	<u>2.5</u>	<u>0</u>	3.5	<u>0</u>	<u>84</u>	2
Comparative Example 2	<u>2.2</u>	<u>0</u>	4.2	<u>0</u>	<u>81.2</u>	2
Comparative Example 3	<u>2.1</u>	<u>0</u>	5.6	<u>0</u>	<u>79.5</u>	2

From Table 4, it can be seen that due to the absence of the pretreatment step of the present invention, the tin oxide content in the passivation film of the tinplates of Comparative Examples 1-3 all exceed the upper limit of 2 mC/cm² defined in the present invention, whereas the tin oxide content in the passivation film of the tinplates of each example of the present invention are relatively low.

In addition, as a result of using the passivation treatment solution of the present invention, the passivation films of the tinplate of the present invention comprise metallic chromium and phosphorus, which are absent in Comparative Examples 1-3. Moreover, the contact angles of Examples 1-9 of the present invention are significantly smaller than those of Comparative Examples 1-3, and the adhesion level of the lacquer film are all Grade 1. These results indicate that the present invention has better surface wettability and lacquer film adhesion performance.

It should be noted that the prior art part in the protection scope of the present invention is not limited to the examples disclosed in the present application. All prior art that does not

contradict the solutions of the present invention, including, but not limited to, prior patent documents, previously published publications, and prior public uses, etc., can be included in the protection scope of the present invention.

Moreover, the combinations of technical features disclosed in this application are not limited to the combinations stated in the claims or in the specific embodiments. All technical features disclosed herein may be freely combined or integrated in any manner, unless such combinations are contradictory.

It should also be emphasized that the above-described embodiments are merely illustrative of the present invention. Clearly, the invention is not limited to these embodiments, and similar modifications or variations that can be directly derived from or readily conceived by those skilled in the art based on the content disclosed in the present disclosure shall fall within the protection scope of the present invention.

Claims

1. A passivation treatment solution for tinplate, wherein the passivation treatment solution comprises the following active ingredients:

chromic anhydride, which has a content of 15-30 g/l;

metaphosphoric acid and/or metaphosphate, which has a content of 5-15 g/l;

ammonium bromide, which has a content of 1-5 g/l;

nitrogen-containing organic compound, which has a content of 0.2-2 g/l.

2. The passivation treatment solution according to claim 1, wherein the nitrogen-containing organic compound comprises at least one of thiourea, glycine and niacin.

3. The passivation treatment solution according to claim 1, wherein the passivation treatment solution has a pH value of 1.2-3.8.

4. A tinplate comprising a steel substrate and a metallic tin layer on the steel substrate, wherein the metallic tin layer has a surface passivation film, and wherein the surface passivation film is formed by the passivation treatment solution according to any one of claims 1-3.

5. The tinplate according to claim 4, wherein the surface passivation film comprises metallic chromium, a trivalent chromium oxide, a tin oxide, and phosphorus, and is free of hexavalent chromium.

6. The tinplate according to claim 5, wherein in the surface passivation film, a content of the metallic chromium is 0.5-2.5 mg/m², a content of the trivalent chromium oxide is 2-7 mg/m², a content of the phosphorus is 0.3-5 mg/m², and a content of the tin oxide is 0.5-2 mC/cm².

7. The tinplate according to claim 4, wherein the tinplate has a lacquer film adhesion level of Grade 1.

8. The tinplate according to claim 4, wherein the tinplate has a surface contact angle of $\leq 76^\circ$.

9. A method for manufacturing tinplate, including the following steps:

a) performing a pretreatment on a tinplate substrate after reflowing to remove tin oxide film on the surface of the tinplate substrate;

b) performing a passivation on the pretreated tinplate substrate, wherein the passivation step includes immersing the pretreated tinplate substrate in the passivation treatment solution

according to any one of claims 1-3, and subjecting the tinplate substrate to cathodic electrolytic treatment as a cathode.

10. The method according to claim 9, wherein the pretreatment includes immersing the tinplate substrate after reflowing in a chromic anhydride solution, wherein the chromic anhydride solution has a chromic anhydride content of 10-20 g/L.

11. The method according to claim 9, wherein the pretreatment is performed for a period of 2-10 s.

12. The method according to claim 10, wherein the chromic anhydride solution has a temperature of 30-50 °C.

13. The method according to claim 9, wherein in step b), the passivation treatment solution has a temperature of 40-65 °C.

14. The method according to claim 9, wherein in step b), the cathodic electrolytic treatment has a cathodic current density of 15-60 C/dm².