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METHOD OF TREATING TIN PLATE OR GALVANIZED SHEET

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ABSTRACT OF THE DISCLOSURE

A process for making tin plate or galvanized sheet which comprises subjecting the electrolytically plated sheet first to a post-treatment with an alkaline solution, then washing the sheet with water, and thereafter subjecting it to an electrolytic passivating treatment in a solution containing (a) a hexavalent chromium ions-furnishing compound and (b) a water-soluble saturated carboxylic acid selected from the group consisting of monobasic fatty acids, dibasic fatty acids, aromatic carboxylic acids, salts of such acids and mixtures of such acid or salts.

Sheets with improved resistance against corrosion and oxidation are obtained.

CROSS-REFERENCES TO RELATED APPLICATIONS

The present application is a continuation-in-part of U.S. patent application Ser. No. 755,803, filed by us on Aug. 28, 1968 and now abandoned.

BACKGROUND OF THE INVENTION

The invention relates to treating tin plate or galvanized sheet, and more specifically to a post-treatment for electrolytically tin plate or galvanized sheet.

The conventional plating processes, for instance for tin plating, comprise electrolytically degreasing a continuous strip of steel, such as a black plate, in an alkaline cleaning solution, followed by pickling in an acid solution; then tinning electrolytically and the surface thus obtained is subjected to flow-brightening the plate. The tin plate is thereafter usually passivated by subjecting it to an electrolytic bath in an aqueous solution containing a hexavalent chromium compound so as to improve its resistance to sulfur-staining, oxidation, discoloration and corrosion.

The results with this process are, however, not quite satisfactory. They are particularly inadequate for cans which are used as containers for protein-rich food containing sulfides, such as meat, fish, shellfish and certain vegetables. The cans then often form a bluish-purple or black tarnish, the so-called sulfur-staining. This staining is caused by the formation of tin sulfides from the sulfur in the food.

Another undesirable staining is caused by the oxidation of tin plate, particularly in cans used for fruit packing.

The reason for all these phenomena is the fact that tin is easily sulfurized and oxidized.

In the conventional treatment to obviate these phenomena, an electrolytic post-treatment was used in a bath containing hexavalent chromium ions. However, this was still inadequate to substantially improve the chemical resistance of the tin plate to the desired extent.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a treatment for tin plate and galvanized sheet which will improve their chemical resistance.

This is accomplished by a first post-treatment, following the electrolytic plating step, with an alkaline solution,

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then washing the plate with water, and thereafter subjecting it to a second post-treatment comprising a passivating treatment in an electrolytic bath containing (a) a hexavalent chromium ions-furnishing compound and (b) a water-soluble saturated carboxylic acid selected from the group consisting of monobasic fatty acids, dibasic fatty acids, aromatic carboxylic acids, salts of such acids and mixtures of such acids or salts. Thus plate or sheet with improved resistance against corrosion and oxidation is obtained.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present process applies to electroplated sheet which is made in the usual conventional manner by degreasing, then, pickling, and thereupon electrolytically applying a tin or zinc coating (more flow-brightening in the case of tin plate). The sheet thus treated is thereafter subjected to an electrolytic bath in an alkaline aqueous solution, the sheet constituting the cathode in this process step. The solution for instance may contain an alkali metal salt, such as an alkali carbonate, alkali borate or alkali phosphate. It may also contain caustic soda or caustic potash instead of the aforementioned alkali metal salts. The concentration of alkali in the solution may range from about 1 g./l. to 30 g./l.

The temperature of the alkaline treatment bath should be between 20 and 70° C., preferably between 40 and 60° C. The treating current should be between 1 and 20 coulombs/dm.² and preferably is between 3 and 10 coulombs/dm.²

The sheet is then subjected to a water rinse. Following this, the sheet is subjected to a second electrolytic post-treatment at a temperature between 30 and 70° C. The bath of this second electrolytic post-treatment contains hexavalent chromium ions and an additive of water-soluble saturated carboxylic acids which may be monobasic fatty acids, such as acetic, propionic and butyric acid, or may be a dibasic fatty acid, such as malonic, succinic, glutaric or adipic acid, or it may be an aromatic carboxylic acid, such as benzoic or phthalic acid. Instead of the acids, the salts of these acids may also be used, and there may also be used a mixture of these acids.

Further examples of useful acids are valeric acid, caproic acid and enanthic acid, illustrating monobasic fatty acids, while pimelic acid, suberic acid, azelaic acid and sebacic acid are further examples of dibasic fatty acids.

The salts of the above acids may be alkali metal salts or ammonium salts.

The sheet will constitute the cathode in the electrolytic treatment in the usual manner. The electric current should be passed through the bath for a period of 0.5 to 5 seconds at a current density of 1 to 10 amps/dm.²

The sheet is then subjected to washing with water and drying.

The concentration of the hexavalent chromium ions in the solution should be between about 2 and 20 g./l. The concentration of the carboxylic acid additive should be between about 3 and 20 g./l. of solution.

If the concentration of acid or its salt falls below the stated minimum amount of 3 g./l. the improvement of the properties of the sheet will not be accomplished. On the other hand, exceeding the upper limit of 20 g./l. is economically undesirable, and in addition also interferes with other properties of the final product.

Without being committed to a specific theory, it is believed that the alkaline treatment in the first stage is effective to activate the tin plate or the galvanized sheet because of the amphoteric properties of tin or zinc. This activation then supports the deposition of a gel-like homo-

geneous non-porous chromate film on the plate or sheet surface formed by the chromate ions together with the carboxylic acid component.

In the conventional processes, it was customary to subject the plated sheet immediately to the passivating treatment with the hexavalent chromium compound because contact of the sheet with any substance such as oils or fats affecting its surface had to be avoided. In the present process, the post-treatment with the chromium compound is effected only after a pre-treatment in alkaline solution. As a result, the process of the present invention produces a highly resistant film on the sheet which will prevent sulfur-staining, oxidation, discoloration and corrosion, and all this is accomplished in a substantially shorter treating period.

The thus-treated tin plate is particularly resistant to sulfur staining and therefore inhibits the formation of black tarnish. In an oxidation test at the temperature of 200° C. for a period of one hour and under conditions of 100% relative humidity at 50° C., the formation of an oxidation film on the sheet was still extremely small. While no increase in the thickness of the chromium film on the plate as compared with the film of a conventionally treated plate could be established and this therefore resulted also in a substantial increase of the solderability of the tin plate.

In the case of the galvanized sheet, the treatment of the invention has the effect of preventing the appearance of the so-called "white rust."

The following examples will illustrate the invention without any intention of limitation.

Example I

A sheet was subjected to conventional electrolytic tin plating. Thereafter it was subjected to the following two-stage electrolytic post-treatment under the following conditions:

First-stage post-treatment:

Na_2CO_3 : 5 g./l.

Treating temperature: 30° C.

Cathodic current density: 6 A./dm.²

Treating time: 1 sec.

After this first-stage post-treatment, the sheet was subjected to a water rinse. There then followed a second-stage post-treatment under the following conditions:

Second-stage post-treatment:

$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$: 20 g./l.

$(\text{CH}_2\text{COOH})_2$: 9 g./l.

Treating temperature: 60° C.

Cathodic current density: 4.5 A./dm.²

Treating time: 1 sec.

The tin plate thus obtained was subjected to the following test: The plate was immersed for one hour in a 40° C. aqueous solution of 5% $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in order to determine the sulfur staining. For the purpose of the test, a graduated scale was used from 0 to 10 to indicate the increasing staining. Tin plate which was not subject to any post-treatment on this scale received the mark 10. Conventionally treated tin plate was ranked 7. The tin plate treated as stated in this example was rated 1. This clearly shows the advance obtained by the treatment of the invention.

In order to test the oxidation properties, the plate was heated for one hour at 200° C. The coulometric reduction was then measured in an aqueous solution of 1×10^{-4} weight percent of HBr. A conventionally post-treated plate showed a result of 3.0 mcoul./cm.², while the plate treated in accordance with the above example showed a result of 0.8 mcoul./cm.². The rate of oxidation accordingly was reduced to about one-fourth that of the conventionally treated plate. Regarding the oxide film existing after a 72 hours exposure to the humidity cabinet test of 100% relative humidity at 50° C., as above men-

tioned, a similar reduction to about ¼ of the comparative value was found to have occurred.

Example II

A sheet which had been electrolytically tin plated in the conventional manner was subjected to electrolytic post treatment under the following conditions:

First-stage post-treatment:

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$: 7.5 g./l.

Treating temperature: 50° C.

Cathodic current density: 4 A./dm.²

Treating time: 1 sec.

Second-stage post-treatment:

$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$: 20 g./l.

$\text{CH}_2(\text{COOH})_2$: 5 g./l.

Treating time: 60° C.

Cathodic current density: 4.5 A./dm.²

Treating time: 1 sec.

The treatment otherwise followed the steps above given and in particular there was a water rinse between the two treatments.

Example III

A tin plate made in the conventional manner was subjected to post-treatment, as in the previous examples, but involving the following conditions:

First-stage post-treatment:

$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$: 7 g./l.

Treating temperature: 50° C.

Cathodic current density: 4 A./dm.²

Treating time: 1 sec.

Second-stage post-treatment:

$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$: 20 g./l.

$\text{C}_6\text{H}_5\text{COOH}$: 5 g./l.

Treating temperature: 60° C.

Cathodic current density: 6 A./dm.²

Treating time: 1 sec.

The plates of both Examples II and III were again subjected to tests regarding sulfur staining which had about the same results as those with the plates treated in Example I.

Example IV

This example illustrates the use of the post-treatment for a zinc plated sheet, or galvanized sheet. This was plated in conventional manner and was then subjected to post treatments in the same manner as in the previous examples under the following conditions.

First-stage post-treatment:

Na_2CO_3 : 2 g./l.

Treating temperature: 50° C.

Cathodic current density: 5 A./dm.²

Treating time: 1 sec.

Second-stage post-treatment:

$\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$: 20 g./l.

$(\text{CH}_2\text{COOH})_2$: 9 g./l.

Treating temperature: 50° C.

Cathodic current density: 10 A./dm.²

Treating time: 1 sec.

The galvanized sheet resulting from these treatments was then subjected to the JIS Z-2371 Salt Spray Test for a time of 24 hours. The sheet did not exhibit any "white rust," as distinguished from a conventionally post-treated sheet, which exhibited a number of white rust spots already after 4 hours' exposure.

This example shows that the present invention when applied to hot-dip galvanized sheet and electrolytic galvanized sheet remarkably improves the property of preventing "white rust."

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by

applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic and specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be protected by Letters Patent is set forth in the appended claims:

1. In a process for manufacturing tin plate or galvanized sheet the steps of making the plated sheet the cathode while immersed in an alkaline electrolyte, passing an electric current through said alkaline electrolyte and plated sheet, washing said plated sheet with water after its withdrawal from said alkaline electrolyte to rinse away any alkaline electrolyte remaining thereon and directly thereafter passivating the washed plated sheet by making the same the cathode while immersed in a solution containing a hexavalent chromium ion furnishing compound and a water soluble saturated carboxylic acid selected from the group consisting of mono basic fatty carboxylic acids, dibasic fatty carboxylic acids, aromatic carboxylic acids, salts of said acids and mixtures of said acids or salts, passing an electric current through said solution and plated sheet whereby a plated sheet having improved resistance to sulfur staining, oxidation, discoloration and corrosion is obtained.

2. Process of claim 1 wherein said alkaline electrolyte comprises a solution containing a member selected from the group consisting of alkali metal carbonates, alkaline borates, alkali metal phosphates and alkaline hydroxides.

3. Process according to claim 1 wherein the treatment in said alkaline electrolyte is carried out at a temperature of from 20 to 70° C. using a current of 1 to 20 coul./dm.².

4. Process according to claim 1 wherein said solution for carrying out said passivating contains hexavalent chromium ions in an amount of between 2 and 20 g./l.

5. Process according to claim 1 wherein said solution for carrying out said passivating contains said water soluble saturated carboxylic acid in an amount of between 3 and 20 g./l.

6. Process according to claim 1 wherein said compound containing hexavalent chromium ion is sodium dichromate.

7. Process of claim 1 wherein said water soluble saturated carboxylic acid is a member selected from the group

consisting of malonic acid, benzoic acid, succinic acid, and alkali metal and ammonium salts thereof.

8. Process according to claim 1 wherein the electrolysis in said alkaline solution is carried out at a temperature of 20 to 70° C. with a current of 1 to 20 coul./dm.², said passivating is carried out at a temperature between 30 and 70° C. for from 0.5 to 5 seconds at a current density of about 1 to 10 A./dm.², said chromium ion furnishing compound is sodium dichromate and is present in an amount of from 2 to 20 g./l. in the passivating electrolyte, said saturated water soluble carboxylic acid is a member selected from the group consisting of malonic acid, benzoic acid, succinic acid, alkaline and ammonium salts thereof and is present in said passivating electrolyte in a concentration of between 3 and 20 g./l.

9. Process according to claim 1 wherein said alkaline electrolyte contains sodium carbonate and the passivating electrolyte contains Na₂Cr₂O₇·2H₂O and (CH₂COOH)₂.

10. Process according to claim 1 wherein said alkaline electrolyte contains Na₂B₄O₇·10H₂O and the passivating electrolyte contains Na₂Cr₂O₇·2H₂O and CH₂(COOH)₂.

11. Process according to claim 1 wherein said alkaline electrolyte contains Na₂HPO₄·12H₂O and said passivating electrolyte contains Na₂Cr₂O₇·2H₂O and C₆H₅COOH.

12. The plated sheet produced by the process of claim 1.

13. Process according to claim 1 wherein said passivating is carried out at a temperature of between 30 and 70° C.

14. Process according to claim 13 wherein said passivating is carried out for from 0.5 to 5 seconds at a current density of 1 to 10 A./dm.²

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