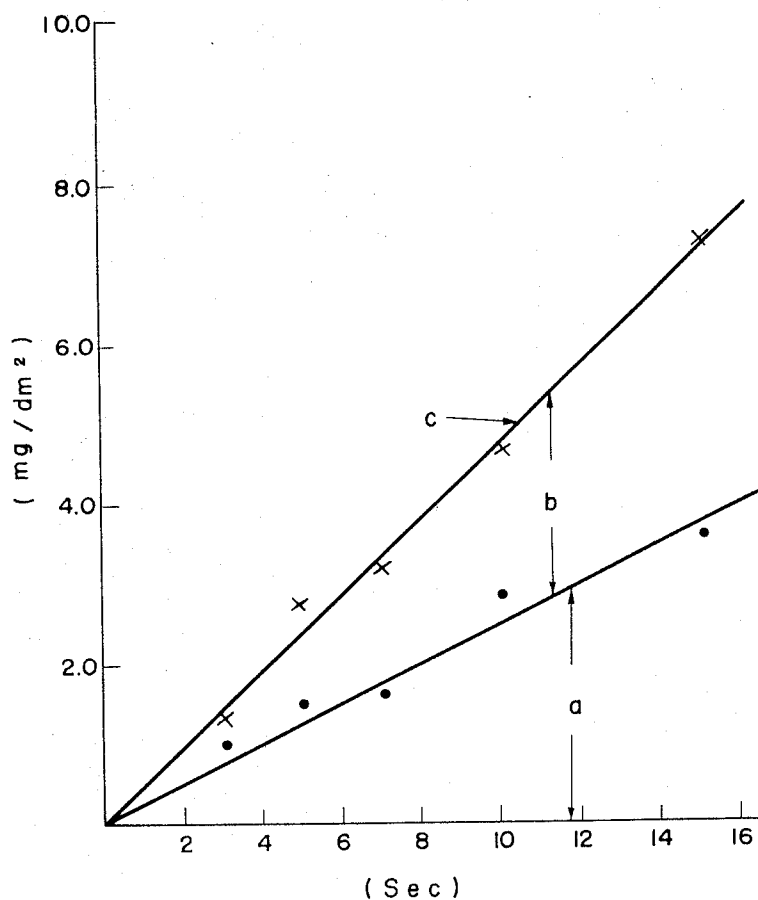


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SHIGERU YONEZAKI ETAL
PROCESS FOR PRODUCING ANTICORROSIVE SURFACE
TREATED STEEL SHEETS AND PRODUCT THEREOF
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3,296,100

PROCESS FOR PRODUCING ANTICORROSIVE SURFACE TREATED STEEL SHEETS AND PRODUCT THEREOF

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3 Claims. (Cl. 204—41)

This invention relates to a process for producing anti-corrosive steel sheets by electrolytically treating steel sheets in a very dilute chromic anhydride-sulphuric acid bath.

Generally, in surface-treated steel sheets made by using a chromic anhydride bath, there are many defects such as, for example, poor paint adhesion, cracking and peeling due to the brittleness of the film formed on the treated steel sheets, and these defects are considered to be caused by the nonmetallic crystalline formation of the film. In order to eliminate such defects, practical electrodeposition processes have been investigated. However, no satisfactory results have yet been obtained.

As a result of long research, the inventors have succeeded in completing the present invention, by which the defects such as are mentioned above can be entirely eliminated.

An object of the present invention is to provide an economical process for producing surface-treated steel sheets which have good corrosion resistance, good paint retention, and good impact resistance.

Other objects of the present invention will become clear from the accompanying drawing and the following specification.

The drawing shows the amount of material deposited in a metallic chromium layer and that of a chemically treated film layer thereon on a steel sheet by electrodeposition according to the method of the present invention depending on the treating time.

The inventors have found that when a steel sheet is electrolytically treated in a dilute aqueous solution of chromic anhydride of a concentration of less than 50 g./l. and having therein a sulphuric acid radical in an amount of 0.2–5% by weight of the chromic anhydride from a sulphate or sulphuric acid, such a surface-treated steel sheet having good corrosion resistance, good paint retention and good impact resistance can be produced at a low cost.

The fact that the concentration of chromic anhydride is limited so that it is less than 50 g./l. is especially important in the present invention. That is to say, only when the concentration of chromic anhydride is limited so that it is less than 50 g./l., will a nonmetallic film be deposited without forming nonmetallic crystals which are considered to be the cause of the defects of steel sheets electrolytically treated with chromic anhydride according to the conventional methods. In other words, only in an aqueous solution of chromic anhydride of a concentration of less than 50 g./l., does the pH value on the surface of the cathode vary so that metallic chromium is electroplated thereon and, at the same time a reduced trivalent chromium compound is deposited on a layer

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of said electroplated chromium. Thus, in the electrolytic treatment according to the present invention two layers will be electrodeposited on a steel sheet: a metallic chromium layer as the bottom layer and a nonmetallic chromate film therein as the outer layer. By forming these two layers surface-treated steel sheets having good corrosion resistance, good paint retention and good impact resistance can be obtained. If the concentration of chromic anhydride is above 50 g./l. there will not be produced the two layers as in the present invention. On the other hand, if the concentration of chromium anhydride is made less than 10 g./l., the consumption of electric power will have to increase, reducing the efficiency of the use of the electricity and further the treatment temperature will have to be reduced, resulting in the formation of an irregular film. Thus, because in an aqueous solution of chromic anhydride of a concentration of less than 10 g./l. such defects as above mentioned will occur, it is preferable to make the concentration of chromic anhydride more than 10 g./l. for a practical operation.

The range of the amount of chromium sulphate to be added to the above mentioned solution or sulphuric acid to be added to the same solution in an amount equivalent to the sulphuric acid radical of said sulphate should be limited to be 0.2 to 5.0% by weight of the chromic anhydride contained in the aqueous solution for the following reasons. If chromium sulphate is added in an amount larger than 5.0% by weight of the chromium anhydride, both the paint adherence and corrosion resistance of the upper nonmetallic chromate film therein will be reduced; but, if it is less than 0.2%, the amount of the sulphuric acid radical will be too small to attain the effect of the present invention.

The object of the present invention can also be attained by using sulphuric acid. However, in this case, the treatment requires more time than when chromium sulphate is used. Therefore, preparatory to the electrolytic treatment a preelectrolytic treatment is to be carried out and the cathode is to be replaced by a new one for the subsequent electrolytic treatment. The quantity of electricity for said preelectrolytic treatment is not critical but, it may be more than 8,000 coulombs/l. by a current density of 10 A./dm.².

The lower the bath temperature, the better the current effect and the thicker the film formed. But, as it is necessary to cool the electrolytic bath and the luster of the film will also decrease, a treating temperature in a range of about 15 to 50° C. is recommended.

Further, the higher the current density, the higher the current efficiency and the higher the corrosion resistance. But, in such case, the color of the film will become blackish and the impact resistance after painting will be likely to be reduced. Therefore, it is necessary to properly select the current density in accordance with the use to be made of the product.

The figure is a diagram showing the relation between the total amount of chromium deposited on the treated steel plate (mg./dm.²) and the treating time in seconds at 40 g./l. of CrO₃, 0.542 g./l. of Cr₂(SO₄)₃ (1.35% of the CrO₃), a bath temperature of 40° C. and a current density of 20 A./dm.². In the figure, (a) shows an electrodeposited layer of metallic Cr as a bottom layer formed on the sample steel sheet, (b) shows a chemically treated coating of nonmetallic chromate compound therein

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formed on the above mentioned metallic Cr and (c) shows a total amount of Cr.

If a steel sheet is treated so as to satisfy such requirements as are mentioned above, the corrosion resistance (as tested in accordance with J.I.S.Z. 2371 (and the paint retention of the steel sheet will be as in Table 1.

TABLE 1.—ANTICORROSIVENESS AND PAINTABILITY

Salt water spray (for 24 hours)	Paintability of ¹ finishing paint (DuPont type impact test)	Paintability and ² lacquerability of inner paint (both adhesion and impact)
Rusting rate 1 to 5%—	No peeling—	Excellent.

¹ A melamine lacquer was applied as the paint.

² A phenolic lacquer was applied as the paint.

Example 1

Chromic anhydride -----g./l. 40
 Chromium sulphate -----g./l. 0.5
 Bath temperature -----° C. 35
 Current density -----A./dm.² 15
 Treating time -----seconds 5

Steel sheets treated under the above mentioned conditions were subjected to salt water spray tests by spraying a solution of 5% NaCl at 35° C. at 20 pounds per square inch, Du Pont type paint adhesion and impact tests, cross-cut tests and drawing tests. The results of these tests are shown in Table 2.

TABLE 2

	Rusting in Salt water Spray tests (24 hr.), percent	Impact tests	Cross-cut tests	Drawing tests
Product (A) of the method of the present invention.	5	No peeling—	Excellent—	Excellent.
Product (B) of the method of the present invention.	2	—do—	—do—	Do.
Thin steel sheet.	100	—do—	—do—	Do.
Commercial steel sheet chemically treated.	5	Peeled substantially on the entire surface.	—do—	Do.

Notes: The product (A) of the method of the present invention was the product in Example 1. The product (B) of the same was a product obtained under the conditions of Example 1 when the current density was 20 A./dm.².

Example 2

Chromic anhydride -----g./l. 20
 Chromium sulphate -----g./l. 0.2
 Temperature -----° C. 30
 Current density -----A./dm.² 15
 Time -----seconds 5

Example 3

Chromic anhydride -----g./l. 10
 Chromium sulphate -----g./l. 0.1
 Temperature -----° C. 20
 Current density -----A./dm.² 10
 Time -----seconds 10

Steel sheets treated in the above Examples 2 and 3 were subjected to Du Pont type paint adhesion and impact tests, cross-cut tests and drawing tests as in the above Table 2. The results were exactly the same as in Table 2.

As demonstrated by the above examples, the feature of the treatment according to the present invention is that the product thereof is excellent not only in corrosion resistance but also in paint adhesion.

Example 4

Chromic anhydride -----g./l. 40
 Sulphuric acid -----g./l. 0.42
 Temperature -----° C. 35
 Quantity of electricity in preparatory electrolysis -----coulombs/l. 8,000

After steel sheets were subjected to the preelectrolytical treatment under the above mentioned conditions, they

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were subsequently electrolytically treated for 5 seconds under the same conditions as in Example 1, with the exception that the cathode used during the pre-electrolytic treatment was replaced with new one. Then, the same favorable results as in Table 2 were obtained.

What is claimed is:

1. A process for producing surface-treated anticorrosive steel sheet, comprising immersing a cathode in a dilute aqueous treating solution consisting essentially of 10–15 g./l. chromic anhydride and a sulphuric acid radical in an amount of 0.2 to 5% by weight of the chromic anhydride in said solution, preliminarily electrolyzing said solution with said cathode to form trivalent chromium ions in an amount of 0.2 to 5% by weight of chromic anhydride in the treating solution, then replacing the cathode with said steel sheet to be surface treated, and then electrolyzing said solution further, whereby an intermediate layer of metallic chromium is first formed on the surface of said steel sheet and a chemically treated layer of non-metallic chromate is then formed thereon.

2. A process for producing surface-treated anticorrosive steel sheet, comprising immersing a steel sheet in a dilute aqueous treating solution consisting essentially of 10–15 g./l. chromic anhydride and a sulphuric acid radical and trivalent chromium ions each in an amount of 0.2 to 5% by weight of the chromic anhydride in said solution, and electrolyzing said solution with said steel sheet as a cathode, whereby an intermediate layer of

metallic chromium is first formed on the surface of steel sheet and a chemically treated layer of non-metallic chromate is then formed thereon.

3. A surface-treated anticorrosive steel sheet having a base of steel, and an intermediate layer of metallic chromium and a surface layer of chromate formed on the steel base by the process comprising immersing a steel sheet in a dilute aqueous treating solution consisting essentially of 10–50 g./l. chromic anhydride and a sulphuric acid radical and trivalent chromium ions each in an amount of 0.2 to 5% by weight of the chromic anhydride in said solution, and electrolyzing said solution with said steel sheet as a cathode.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No 3,296,100

January 3, 1967

Shigeru Yonezaki et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, lines 10 and 24, for "15", each occurrence,
read 50

Signed and sealed this 26th day of September 1967.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents