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CHROMATE PROCESS

Rihei Tomono, Ukyo-ku, Kyoto, Japan, assignor to Okuno Chemical Industry Company, Osaka, Japan

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1 Claim. (Cl. 148—6.16)

This invention relates to an improvement in the chromate process which is employed in the art for elevating the corrosion resistance of articles electroplated with zinc or cadmium and of zinc die castings. More particularly, the invention pertains to a method wherein a salt of titanium is dissolved in the chromate bath and the article to be treated is dipped in the bath.

According to the chromate process employed in the art, the article to be treated is dipped at room temperature or at elevated temperatures in a bath containing a hexavalent chromium compound and an organic or inorganic acid to form a chromate deposit on the surface of the article. The chromium compound employed, for example, can be chromic acid anhydride, potassium bichromate, sodium bichromate and the like. Details of the process are disclosed in Electroplating Engineering Handbook (Reinhold Publishing Corp., 1955, pp. 366 to 376), and the property and composition of the chromate deposit in L. F. Spencer, Metal Finishing (vol. 158, No. 1, pp. 58 to 65), W. E. Pocock, Metal Finishing Guidebook (1960, pp. 512 to 524), and S. L. Sisler, J. Dass & M. A. Henderson, Plating (vol. 41, No. 2, p. 147). Generally speaking, the integral components of the bath are CrO_3 or an alkali bichromate and sulfuric acid. The article to be treated is dipped in the bath at 20° to 65° C. for 3 to 5 seconds. The article is then suspended in the air at room temperature for a short period of time, washed with water and dried.

The improved process of this invention comprises dissolving one of the titanium salts, titanous phosphate, titanous sulfate, titanic sulfate and titanyl sulfate in the ordinary chromate bath, and dipping the article to be treated in the resultant bath in an identical manner as employed in the conventional chromate art. There are no specific changes made in the composition of the starting chromate bath. The pH of the bath is kept at below 1.5 in order that the desired amount of the titanium salt satisfactorily dissolves in the bath. A bath containing 80 to 400 grams per liter of chromic acid and 5 to 60 grams per liter of sulfuric acid is expedient. The titanium compound employed in this invention can be titanous phosphate, titanous sulfate, titanic sulfate and titanyl sulfate. The most desirable amount of titanium salt dissolved in the bath ranges from 0.5 to 15 grams per liter. 30 grams per liter or more of titanium salt damage the adhesive power of the deposit.

The principle of this invention is put into practice in the following manner:

A zinc-plated article, for instance, is dipped in the acidic bath of this invention containing hexavalent chromium salt and titanium salt. Then the zinc contained in the deposit starts being oxidized and dissolving into the bath, allowing the zinc still remaining undissolved in the deposit to be sufficiently activated and replaced electrochemically with the titanium salt, yielding a layer of titanium, probably of titanium hydroxide, on the surface of the zinc deposit. The hexavalent chromium salt in oxidizing the zinc deposit, on the other hand, is reduced to trivalent chromic oxide and deposits in the state of a gel on the titanium layer, absorbing titanium salt, hexavalent chromium salt and acid used in the chromate bath. The article is then suspended in the air at room temperature for about 5 seconds and dried at 50° to 80° C. The layer or deposit thus obtained is hard and compact, and the brilliancy and corrosion resistance are markedly improved as compared with the article conventionally chromated.

The metals which can be treated directly or indirectly with the method of this invention include iron, zinc, cadmium, copper, brass, aluminum, bronze, silver, magnesium and the like. Said metals can all be treated in the same manner as described above, yielding a satisfactory and much improved corrosion resistance, although the replacement with the titanium salt in the bath does not take place with the metals having higher electrochemical activity than titanium.

To have a better understanding of this invention, preferred examples of the same are disclosed below:

Example 1

A soft iron article (10 cm. x 10 cm. x 0.04 cm.) is electrochemically plated with zinc according to the conventional method. More particularly, 42 g./l. of ZnO, 92 g./l. of NaCN and 40 g./l. of NaOH are dissolved in water. Electric current is applied in the order of 3 amp./dm.^{2} in terms of cathode current density, and the article is dipped in the bath at 18° to 20° C. for 25 to 30 minutes to be electrochemically plated with a zinc deposit 20 microns thick. The article is then washed with water, dipped for 2 seconds in an aqueous solution containing 0.5 weight percent of nitric acid, and dried in the air.

The zinc-plated article is then dipped at 20° to 30° C. for 5 seconds in the bath of this invention containing 200 g./l. of CrO_3, 10 g./l. of $TiOSO_4 \cdot 2H_2O$ and 20 g./l. of H_2SO_4. The article thus treated is suspended in the air for 5 seconds, washed with water, and dried in the air at 70° C. for 5 to 6 hours. As compared to a control article which is prepared in an identical manner as described above without $TiOSO_4 \cdot 2H_2O$, the brilliancy of the article treated with the titanium bath of this invention is more pronounced than that of the control article but with no substantial difference in the color.

To ascertain the presence of titium salt, the sample article is dipped in dilute sulfuric acid to dissolve the titanium layer, and 2 cc. of 3 percent hydrogen peroxide are added to the resulting solution and agitated. Then the solution turns yellow in confirmation of the presence of titanium salt. Control article is also treated in the same manner, but the solution remains unchanged in color.

Sodium carbonate is also employed in amount of 30 g./l. to decolor the layer, and the layer is subjected to the same test as above, yielding the same result.

When subjected to the Cass Test (Metal Finishing, vol. 57, No. 12, (1959)) and Corrodkote Test (Proc. Am. Electroplaters Soc., vol. 43, No. 50 (1956)), the corrosion resistance of the sample article is found 3 to 5 times more than that of control.

The brilliancy of the layer decolored in an alkaline bath is damaged when $TiOSO_4 \cdot 2H_2O$ is employed in amount more than 16 g./l. in the bath of this invention.

Example 2

A soft iron article of the same size as employed in Example 1 is electrochemically plated with cadmium.

More particularly, 32 g./l. of CdO and 75 g./l. of NaCN are dissolved in water. Electric current is applied in the order of 1 amp./dm.^{2} in terms of cathode current density, and the article is dipped in the bath at 18° to 20° C. for 50 minutes to be electrochemically plated with a cadmium deposit 20 microns thick. The article is then treated with the same bath and in the same manner as employed in Example 1, yielding a uniform titanium layer containing chromate on the surface of the article. 5 percent NaCl is then sprayed on the article to measure the period of time required for decomposing the deposit into an opaque rust. Findings are as follows:

	Sample 1, hr.	Sample 2, hr.	Sample 3, hr.
Article treated with the bath of this invention	288	312	288
Article conventionally chromated	96	96	96

It is our intention that the invention be not limited by any of the details of description unless otherwise specified, but rather be construed broadly within the spirit and scope of the invention as set forth in the the accompanying claim.

What is claimed is:

A method of producing a corrosion resistant coating upon a metal article having a surface selected from the group consisting of zinc and cadmium which comprises dipping such article in an aqueous chromating bath of pH below 1.5 consisting of an aqueous solution of 0.5 to 30 grams per liter of a titanium compound selected from the group consisting of titanous sulfate, titanic sulfate, titanyl sulfate and titanous phosphate and 80 to 400 grams per liter of chromic acid, suspending the dipped article in air, washing the article with water, and drying the article at a temperature between 50° and 80° C.

References Cited by the Examiner

UNITED STATES PATENTS

2,786,002	3/57	Van et al.	148—6.2
2,798,830	7/57	Newhard et al.	148—6.2
2,851,385	9/58	Spruance et al.	148—6.2

RICHARD D. NEVIUS, *Primary Examiner.*