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[54] **METHOD OF TREATING SURFACES OF STEEL PRODUCTS**

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[63] Continuation-in-part of Ser. No. 775,802, Nov. 14, 1968, abandoned.

[30] **Foreign Application Priority Data**

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[58] **Field of Search** ..... 204/33-34, 32, 29, 141, 56, 58, 41, 51, 56 R, 28

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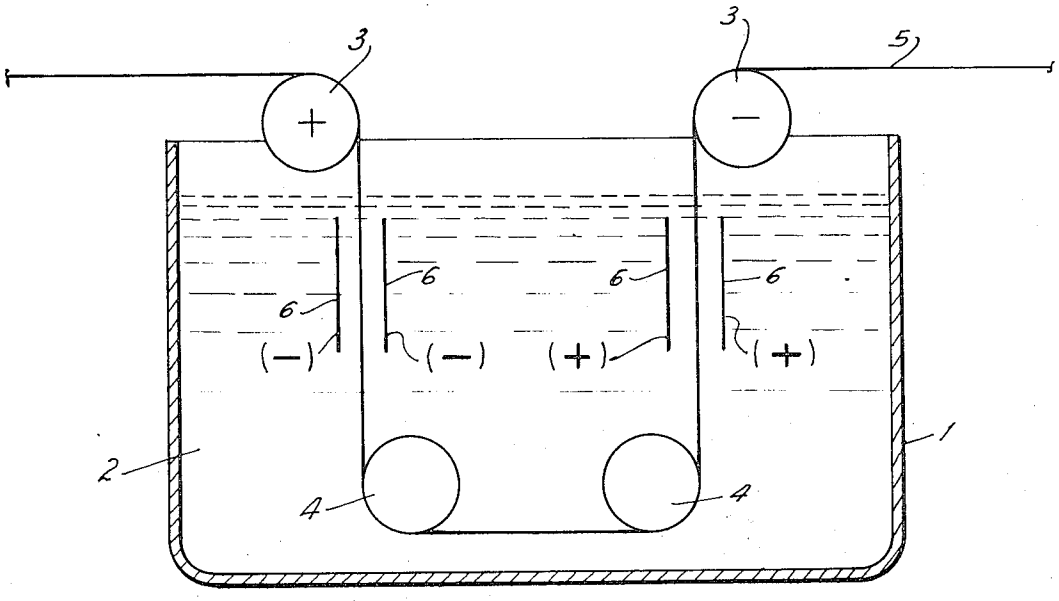
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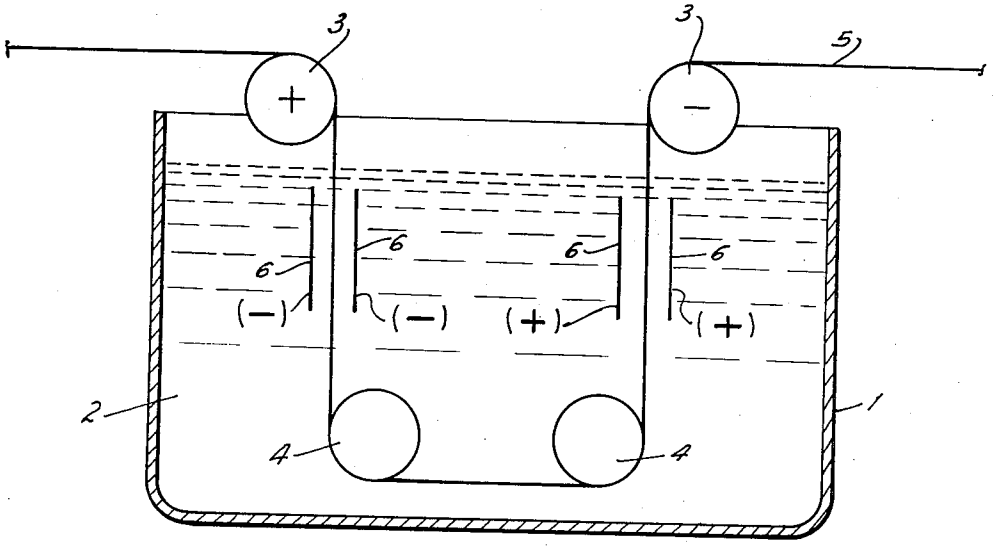
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[57] **ABSTRACT**

Method of treating the surfaces of metal products to provide protection against corrossive attack, comprising the steps of treating such metal products anodically in an aqueous electrolyte consisting of hexavalent chromium ions and borate ions and thereafter treating said metal products cathodically in an aqueous electrolyte consisting of hexavalent chromium ions and borate ions.

10 Claims, 1 Drawing Figure




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METHOD OF TREATING SURFACES OF STEEL PRODUCTS

This application is a continuation-in-part of application Ser. No. 775,802, filed Nov. 14, 1968 and now abandoned.

The present invention relates to a method for treating the surfaces of steel products, metal plated steel products and non-ferrous metal products to improve the corrosion resistance properties thereof in a shorter treatment period.

The method of this invention is of the so-called electrolytic chromate treatment type of process. A number of patents have been issued directed to the conventional electrolytic chromate treating procedures utilizing chromic acid and boric acid including U.S. Pat. Nos. 2,733,199 and 2,370,592 and Japanese Pat. No. 268,837.

The first two described procedures require more than 10 seconds for the treatment time making it very difficult to treat metal articles continuously and quickly for imparting corrosion resistance thereto. According to the last method, a coating of crystalline phosphate and gel-like chromate is deposited on a metal surface by cathodic electrolytic treatment. This coating is converted easily into a chalk-like film so that it is then very hard to form a hydrated homogeneous chromium oxide film from the electrolyte containing phosphoric acid. This has the result that the corrosion resistance provided by the coating is very poor.

This invention has as its object avoiding the above mentioned disadvantages.

Another object of this invention is to provide a method for improving corrosion resistance properties of metal surfaces adapted to be carried out continuously and rapidly.

These and other objects and advantages of the invention will become apparent from a consideration of the following disclosure.

In accordance with the invention it has now been found that if a metal product is anodically treated in an aqueous electrolyte containing hexavalent chromium ions and borate ions and thereafter treated cathodically in an aqueous electrolyte containing hexavalent chromium and borate ions, a stable film is formed on the metal surface in a shorter treatment time.

A complete understanding of the invention may be had from the following detailed description and explanation which refer to the accompanying drawing illustrating the preferred practice. The drawing shows diagrammatically an apparatus for carrying out the surface treatment process of the invention.

Illustrative of the preferred hexavalent chromium compounds which can be used in accordance with the invention, there may be mentioned chromic acid, alkali metal chromate, ammonium chromate, alkali metal dichromate, ammonium dichromate and the like.

Among the preferred borate compounds which may be used are boric acid, boric anhydride, alkali metal borate, ammonium borate and the like.

The concentration of the hexavalent chromium ions in the electrolyte can vary within the range of from 3 to 50 g/l. When the concentration of the hexavalent chromium ions is less than 3 g/l, the improved and desired properties in the coating film which is obtained will not be realized. When the concentration exceeds 50 g/l, the hydrated chromium compounds deposited on the metal surface dissolve easily and a stable and uniform coating does not result. The concentration of the compound which is converted into borate ions in the electrolyte may range from 5 to 50 g/l. When the concentration of the borate compound is less than 5 g/l, the depositing power for effecting coating of the resultant electrolyte is poor and the properties of the coating are unsatisfactory. Further, when the concentration of the borate compound exceeds 50 g/l, the borate compound does not dissolve easily in the electrolyte and is easily separated out therefrom.

A further important aspect of the process of the invention is that the metal surface is first subjected to treatment anodically in the electrolyte containing the hexavalent chromium and borate ion and thereafter is cathodically treated in the same electrolyte. If the metal surface is treated using only one of the steps, i.e., anodic or cathodic treatment steps or if the metal surface is subjected to cathodic treatment first, that is if the anodic treatment is carried out following the cathodic treatment, the improved properties resulting from the high coating power, high current efficiency and high corrosion resistance are not obtained. Moreover, it has been found by experiment that only by a process in which the metal surface is treated cathodically directly after the anodic treatment is there obtained a clear coating on the metal surface. More particularly the experiments have established that the anodic treatment step removes oxide and any other contaminants from the metal surface being treated and only then is the improved coating formed by the cathodic treatment step. Further it has been found from the experimental data that a coating formed from the electrolyte at about room temperature tends to be nonuniform and is only poorly structured so that it is necessary to heat the electrolyte in order to avoid such difficulties. However, if the electrolyte is heated to a temperature in excess of 80° C, the loss of electrolyte by evaporation becomes quite marked and is not desirable from an economical point of view. Generally speaking in the electrolytic chromate treatment with the use of increasing temperatures, the electrical current efficiency of the electrolyte and the corrosion resistance properties of the coating are decreased. It has been found that the temperature of the treating electrolyte is most advantageously maintained at about 30° to 80° C and preferably at between 40° and 50° C.

The pH range to be maintained in the electrolyte varies according to the type of metal to be treated. Generally a pH of from zero to six is used. In the case of steel surfaces, pH values at the lower end of the range and desirable. However, in the case of aluminum, zinc and tin surfaces, if the pH of the electrolyte as used is too low, the metal surface will undergo dissolution and there is the danger of resultant impairment of the properties of the surface, so that in this instance, higher pH values are desirable. The pH value of the electrolyte can be regulated and maintained by addition of an alkali metal hydroxide or chromic acid as indicated.

The current density and treating period are interrelated both being dependent one on the other. Thus when a metal surface is treated at high speed, a high current density and a shorter treating period should be utilized. In treating a metal surface by the method of this invention, it is easy to select proper current densities by considering the treatment period involved. The preferred anode treating current amounts to between 0.1 coul/dm^2 and 30 coul/dm^2. It is advantageous to se-

lect a suitable current density according to the type of metal and the other treating conditions. The cathodic treatment follows the anodic treatment step and the cathodic current density in the second step amounts to between 1 coul/dm² and 300 coul/dm². The current density selected should take into consideration the type of metal involved, the anodic treating current which has been used and the other treatment conditions. The treatment times for the aforesaid current ranges generally amounts to between 0.2 seconds and 10 seconds for each treatment step, although of course in selecting the treatment time, consideration must be given to the speed at which the metal article is moving through the apparatus.

In order to show the criticality of the two treatment steps and namely a preliminary anodic treatment step followed by a cathodic treatment step, samples of tinplates steel were subjected to cathodic treatment alone and to a combination of both anodic and cathodic treatments. The results and details of such treatment are set out in the Table which follows:

Comparing electrochemical coating of tin plated steel in one and two steps

Composition of anodic treating solution, g./l.	Composition of cathodic treating solution, g./l.	A: Amount of adhering chromium, mμ g./cm.²	A: Amount of high temperature oxidized film, m.coul./cm.²	B: Penetrating test of 5% Na_2S $9H_2O$
No anodic treatment	20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$	0.55	2.3	7
20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$	20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$	3.01	0.42	1
No anodic treatment	20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$+25 g./l. H_3BO_4	0.60	2.0	7
20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$+25 g./l. H_3BO_4	20 g./l. $Na_2Cr_2O_7 \cdot 2H_2O$+25 g./l. H_3BO_4	0.73	0.33	1

Additive	pH	Polarity	Oxidized film, 200° C./1 hr. heating, mc./cm.²	Sulfur stain test, 5% Na_2S, 40° C./1 hr., rating	Humidity cabinet test (coulometric determination of oxide) 98% 50° C., 72 hr., cm./cm.²	Appearance
None	4.13	Cathodic	1.74	6	9.12	Unchanged.
Do	4.13	Anodic-cathodic	1.08	4	3.67	Tin crystal.
HBF_4, 0.5	2.37	Cathodic	1.68	6	7.26	Unchanged.
HBF_4, 0.5	2.37	Anodic-cathodic	1.08	4	4.13	Tin crystal.
HBF_4, 3.0	1.68	Cathodic	1.21	5	11.22	White.
HBF_4, 3.0	1.68	Anodic-cathodic	1.07	5	8.07	Do.
H_2SiF_6, 0.5	2.35	Cathodic	1.53	6	7.50	Unchanged.
H_2SiF_6, 3.0	2.35	Anodic-cathodic	1.02	5	4.23	Tin crystal.
H_2SO_4, 0.17	2.53	Cathodic	1.86	6	7.16	Unchanged.
H_2SO_4, 0.17	2.53	Anodic-cathodic	0.93	4	3.54	Tin crystal.
H_3BO_4, 2.5	2.50	Cathodic	2.00	7	9.81	Unchanged.
H_3BO_4, 2.5	2.50	Anodic-cathodic	0.33	1	0.40	Do.

A Tin plated steel was heated in air at a temperature of 200+3° C for one hour, the tin oxide formed in such a time cathodically electrolyzed for reduction in an HBr aqueous solution, and the amount of the oxidized film determined.

B Tin plated steel was immersed in 5 percent Na_2S. $9\text{-}H_2O$ at a temperature of 40°C for one hour and the sulfide staining discoloration evaluated as falling into one of 11 classes of from zero (no staining) to 10 (heavy staining).

Comparison of the results set out in the Table shows that much better corrosion resistance is achieved when an anodic treatment preceeds the cathodic treatment. Moreover, the comparison clearly establishes that the addition of boric acid to the chromate solution is by itself not sufficient to produce a satisfactory film and that for full protection, the preceeding anodic treatment is required. Although the entries would appear to indicate that some degree of protection can be obtained without the use of boric acid it should be noted that the film produced by the treatment without using the same was more than four times as thick as that produced in the treatment in accordance with the invention where the same was used.

In order to further emphasize the importance of the presence of the borate ions in the electrolyte in the process of the invention a further series of Experiments was carried out.

A basic electrolyte solution containing only chromate ions was prepared which was modified as hereinafter indicated and tin plated steel strips then subjected to both anodic and cathodic treatment as follows:

Main agent	: $Na_2Cr_2O_7 \cdot 2H_2O$	20 g/l
Bath temperature	: 50°C	
Cathodic current density	: 4.0A/dm²	
Anodic current density	: 0.2A/dm²	
Cathodic treating time	: 1 sec.	
Anodic treating time	: 1 sec.	

The data and results can be seen from the Table set out on the following page:

The above Table clearly shows that when both an anodic and cathodic treatment was carried out, the appearance was not markedly affected by the presence or absence of the borate ions. However, when both steps and the sequence thereof were followed, the presence of the borate ions had a considerable effect on the resistance to sulfur staining and oxidation.

A more complete understanding of the invention may be obtained from the following detailed description and explanation which refer to the accompanying Drawing illustrating the preferred practice. The Drawing shows diagrammatically the two steps of the invention and apparatus used for performing it.

Referring in detail to the Drawing, the reference numeral 1 designates an electrolytic cell containing electrolyte 2. The cell is fitted with conductor rolls 3 mounted above deflector rolls 4 for guiding the steel strip 5 which is fed in the direction shown by the arrow. The conductor rolls 3 lead the strip to the deflector

rolls 4 and into the cell 1, drawing it off therefrom. At the point where the strip 5 is dipped into the electrolyte 2, insoluble electrode plates 6 are installed as counter electrodes. On the down pass side, the counter electrodes are made the cathode with respect to the strip 5 which then serves as the anode and on the up pass side, the counter electrodes constitute the anode with respect to the strip 5 which now serves as the cathode. The counter electrodes therefore serve as cathode and anode with respect to the strip 5 and are arranged respectively on both sides of the strip in the electrolyte so that the strip passes therebetween and is treated first anodically and then cathodically in a continuous manner. The periods of anodic treatment and cathodic treatment may be freely regulated by shortening or lengthening the length of the counter electrodes and by use of auxiliary cells arranged prior to or after the cell 1.

The following Examples serve to illustrate the invention but are in nowise to be construed as limiting the scope thereof.

Example 1

A previously degreased and pickled steel strip was treated under the following conditions:

Chromic acid	50 g/l
Borax	30 g/l
Treating temperature	50°C
Anodic treating current density	10 A/dm²
Anodic treating time	1 sec.
Cathodic treating current density	20 A/dm²
Cathodic treating time	4 sec.

The coating film obtained was blue-yellow in color. The thusly treated steel was exposed for 6 hours to the conditions of the JIS Z-2371 salt spray test. On examination, it was found that the steel sheet was free of ferric rust while an untreated steel sheet exposed to the same conditions showed ferric rust over substantially the entire surface thereof after 5 minutes of exposure. Phosphate treated steel evidenced ferric rust formation after only about 30 minutes of exposure. A previously degreased and pickled steel strip was then treated in the same electrolyte under the following conditions:

Cathodic current density	20 A/dm²
Treating time	4 sec.

The coating film thereby obtained, i.e., by cathodic treatment alone was blue-yellow and showed evidence of ferric rust after only 3 hours of exposure.

Example 2

An aluminum plated steel strip was treated under the following conditions:

Chromic acid	50 g/l
Boric acid	40 g/l
Treating temperature	40°C
Anodic treating current density	0.5 A/dm²
Anodic treating time	1 sec.
Cathodic treating current density	20 A/dm²
Cathodic treating time	6 sec.

The coated film thusly obtained was grey-white and after exposure for 120 hours to salt spray in accordance with the test procedure of JIS Z-2371 did not show any white rust formation while an untreated aluminum plated sheet showed white rust after only 2 hours of exposure.

Example 3

A galvanized sheet strip was treated under the following conditions:

Sodium dichromate	20 g/l
Borax	20 g/l
pH adjusted to 4.0 by adding chromic acid	
Anodic treating current density	0.2 A/dm²
Anodic treating time	1 sec.
Cathodic treating current density	6 A/dm²
Cathodic treating time	2 sec.

The coated film which was obtained was clear and after treatment and exposure for 24 hours to salt spray (JIS Z-2371) still did not show any white rust while an untreated galvanized sheet showed white rust after only 1 hour of exposure.

Example 4

A tin plated strip (No. 25) was treated under the following conditions:

Sodium chromate	20 g/l
pH adjusted to 2.5 by adding of chromic acid	
Anodic treating current density	0.7 A/dm²
Anodic treating time	1 sec.
Cathodic treating current density	4 A/dm²
Cathodic treating time	1 sec.

The coated film thereby obtained was colorless and clear. After the treated tin plate had been exposed for 6 hours in a humidity cabinet under conditions of 100 percent relative humidity and a temperature of 50° C, it did not show any evidence of ferric rusting while an untreated tin plate (No. 25) showed ferric rust after only 30 minutes of exposure.

As has been set out above, according to the instant invention, highly corrosion resistant tin plate is obtained. Moreover, the tin plate as treated in accordance with the invention is highly resistant to oxidation and sulfide staining. The oxidation resistant properties are evidenced in that a tin plate treated in the foregoing process has an oxide film value of about 0.1 mcoul/cm² when the oxide value is determined after 3 months of storage at room temperature and measured by a coulometric reduction procedure while a conventionally treated tin plate has a value of 3 mcoul/cm² under the same conditions.

Cans manufactured in the conventional manner from the tin plate produced in accordance with the above Example were packed with boiled mackeral and stored at approximately 50° C. After one month's storage the cans did not show any sulfide staining and the rating number for the staining amounted to zero when measured under a scale of discoloration calculated on the basis of 11 stages, zero representing no staining and 10 heavy staining. Cans manufactured from the conventional tin plate had rating values of seven under the same conditions.

The tin plate strip was also treated in the same electrolyte under the following conditions:

Cathodic current density	4 A/dm²
Treating time	1 sec.

The coated films thereby obtained using cathodic treatment alone was colorless and clear and the treated tin plate showed ferric rust after 2 hours in the humidity cabinet test under conditions of 100 percent humidity and a temperature of 50° C. the sheets had an oxide film value of 2.5 mcoul/cm² after 3 months of storage

at room temperature. Cans prepared from this cathodic treated tin plate had a rating of six in the sulfur staining test after one month of storage under the conditions as set out above.

According to the invention the metal surface treatment is carried out in a very short period of time and results in uniform hydrated chromium films whereby there is realized a markedly improved corrosion resistance. It is further evident that the oxidation resistance properties and sulfide staining discoloration resistance properties which are required in connection with plate used as canning materials are substantially improved making the instant invention for treating metal surfaces a considerable contribution to the industry.

We claim:

1. A method of applying a corrosion-resistant coating to a metal article which comprises the steps of immersing the article in an aqueous electrolyte bath consisting essentially of a mixture of hexavalent chromium ions in a concentration between 3 and 50 grams per liter and borate ions in a concentration between 5 and 50 grams per liter, the said electrolyte being maintained at a pH value between 0 and 6.0, electrolyzing the said article immersed in the said electrolyte first anodically until the current applied is between 0.1 and 30 coulombs per square decimeter and then cathodically until the desired corrosion-resistant coating is formed.

2. A method of treating metal products as described in claim **1** wherein the hexavalent chromium ions are present in said electrolyte in a concentration of 3 to 50 g/l.

3. A method of treating metal products as described in claim **1** wherein the concentration range of borate compounds which provide borate ions in said aqueous electrolyte is between 5 and 50 g/l.

4. A method as defined in claim **1** in which the metal article consists of a metal strip and the strip is electrolyzed in the bath by being passed between two counter electrodes that are immersed in the bath, the first of which serves as an anode and the second of which serves as a cathode with respect to the strip.

5. A method as defined in claim **1** in which the electrolyte is maintained at a temperature between 30° and 80° C.

6. A method of treating metal products according to claim 1 wherein the electrolyte is maintained at a pH value of from zero to six.

7. A method as defined in claim **1** in which the current applied during the cathodic electrolysis is between 1 and 300 coulombs per square decimeter.

8. A method of treating metal products as described in claim **1**, wherein said metal products are treated anodically by the passage of between 0.1 and 30 coul/dm^2 and subsequently treated cathodically by passage of between 1 and 300 coul/dm^2.

9. A method as defined in claim **1** in which the electrolytic bath contains 20 grams per liter of sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) and 25 grams per liter of boric acid (H_3BO_3).

10. A process as defined in claim **4** in which the metal article is a tin-plated steel sheet material.

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