United States Patent [19]
Hart

[11] 3,766,023
[45] Oct. 16, 1973

[54] COLORING STAINLESS STEELS

[75] Inventor: Anthony Christopher Hart, Dudley, England

[73] Assignee: The International Nickel Company, Inc., New York, N.Y.

[22] Filed: May 11, 1972

[21] Appl. No.: 252,459

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 114,357, Feb. 10, 1971.

[30] Foreign Application Priority Data

May 26, 1970 Great Britain 25215/70
Jan. 11, 1971 Great Britain 1245/71

[52] U.S. Cl. ..... 204/38 B, 204/51, 148/6.21
[51] Int. Cl. C23f 17/00, C23b 5/06
[58] Field of Search ..... 148/6.21; 204/29, 204/56, 51, 38 B, 41, 38 A, 42

[56] References Cited

UNITED STATES PATENTS

3,535,213 10/1970 Okada 204/29

Primary Examiner—John H. Mack
Assistant Examiner—R. L. Andrews
Attorney—Ewan C. MacQueen et al.

[57] ABSTRACT

Films or coatings on corrosion resistant chromium-containing alloys, e.g., stainless steel produced by immersion in solutions of chromic acid, are electrolytically treated to increase the coating's resistance to abrasion. In the electrolytic treatment, the coated chromium-containing metal is made the cathode in a bath capable of depositing metallic chromium and the treatment is conducted for a time and under cathodic conditions insufficient to produce a visible white deposit of metallic chromium.

9 Claims, No Drawings

COLORING STAINLESS STEELS

The present application is a continuation in part of U.S. application, Ser. No. 114,357 filed Feb. 10, 1971.

This invention is directed to an electrolytic hardening treatment for films or coatings on corrosion resistant chromium-containing alloy, e.g., stainless steel and to the product produced thereby.

The natural finish of stainless steel as it comes from the mill is quite attractive and, in most cases, that is the state in which this material has been utilized. For some purposes, architectural applications, for example, colored stainless steels would be desirable to achieve additional variety in the visual impact of this material. A number of proposals exist, therefore, for coloring stainless steel, among them the processes described in British Pat. Nos. 1,122,172 and 1,122,173, both published July 31, 1968. In accordance with these British patents, the stainless steel is immersed in an aqueous solution of chromic acid which also contains sulfuric acid and, in the latter of these patents, also containing manganous sulfate. Thus, the British patents disclose that the coloring bath may contain CrO_3 in an amount between 50 and 1,000 g/l (grams per liter) of water, and can be further acidified with sulfuric acid in amounts up to 600 g/l. A preferred ratio of the weights of CrO_3 to sulfate ion added as sulfuric acid is from about 100:1 to about 1:1, although in some cases the ratio can extend to 1:2. An addition of manganous sulfate ($MnSO_4.4H_2O$) in an amount in the range of 0.3 g/l to 50 g/l, e.g., 4 to 5 g/l, speeds the formation of the colored films. The bath temperature should be in the range from about room temperature up to about 100°, e.g., 70° C. Blue, yellow, red, greenish-red and gold films have been produced on stainless steels by this immersion process. In addition, it is disclosed that a so-called "terminal gold" color can be produced by immersion in the above-described solutions, e.g., a chromic acid-sulfuric acid bath at a temperature of 65° to 75° C. containing 520 g/l to 580 g/l of CrO_3 and a CrO_3-sulfate ion ratio of from 3:1 to 7:1, which color is not changed by increasing the period of immersion. It is possible, however, to obtain blue to red colored films from such "terminal gold" film by heat treating in air at a temperature of from 300° to 700° C.

In the production of colored films, the steel must be left in the solution for a specific period of time before any recognizable color appears on the surface. We have found, however, that some film is formed on the surface of the steel before any color is detectable, the steel retaining its natural appearance. It is likely that the color is caused by interference effects produced only when a certain thickness of film is reached, these effects and therefor the colors, varying with the thickness of the film. In a variation of the immersion coloring process, electric current applied so as to make the object being colored anodic, can be used to assist in the coloring operation. Such a variation was disclosed by C.E. Naylor in an article which appeared in Plating, Vol. 37, No. 2, February, 1950, page 153 et seq. According to Naylor, the coatings produced galvanically or electrolytically as well as by immersion are oxidic and exhibit colors which are due to interference effects.

The corrosion resistance of stainless steel, whether austenitic or ferritic, is well known but nevertheless susceptible of improvement. One object in the invention is to improve this resistance. Our main object is to

improve the resistance of colored stainless steel to both corrosion and abrasion.

Other objects and advantages of the invention will become apparent from the following description.

According to the invention, a film is produced on the surface of a corrosion-resistant, chromium-containing alloy, e.g., stainless steel, by treatment with an aqueous solution of chromic acid with or without other constituents, and the steel bearing the film is then subjected to a short electrolytic treatment. This treatment comprises making the alloy the cathode in a bath of an electrolyte from which chromium can be deposited, e.g., an aqueous solution of chromic acid and sulfuric acid for a period of time which depends upon the concentration of the bath, the current density and the temperature, but which is always at least one minute, though not so long that any chromium becomes visible on the colored surface as a white deposit. It is desirable to make the current density low, because it is then more easily possible to stop the process at the right time by visual observation.

It is found that by means of the invention stainless steel treated by the aqueous solution to form both colored and uncolored (that is to say, natural colored) steels are rendered more resistant to corrosion by the application of the cathodic treatment and the resistance to abrasion of colored steels is much improved.

Coloring may preferably be achieved by immersing the stainless steel in a hot aqueous solution containing chromic and sulfuric acids, the composition and temperature range being as follows:

	Range	Advantageous	Optimum
CrO_3 concentration	200–400 g/l	240–300 g/l	300 g/l
H_2SO_4 concentration	350–700 g/l	450–550 g/l	550 g/l
Temperature	65–80°C.	68–72°C.	70°C.

The coloring treatment can be successfully operated over wide limits of solution concentration and temperature, but in order to achieve reproducibility of results and good color matching it is necessary to ensure that these variables and also the time of immersion are closely controlled. Under the optimum conditions coloring takes between about 7 and 15 minutes, depending on the shade desired. At lower temperatures, the time required for coloring is lengthened, while at higher temperatures, the time is shorter and consequently color control may be difficult. Under the optimum conditions a useful uncolored film is formed in about 5 minutes, a blue film in about 8 minutes and a gold film in about 10 minutes. It is surprisingly found that if the steel is in the martensitic state, the coloring treatment turns its black.

An alternative method of control, based upon measurement of potential difference beteeen the item being colored and a reference electrode is disclosed in U.K. Provisional Applications Nos. 29229/71 and 17940/72 filed in the name of Skedgell et al.

The cathodic treatment of the film-bearing stainless steel is most advantageously carried out in an electrolyte containing 250 g/l CrO_3 and 2.5 g/l sulfuric acid at a temperature of 40° C. The most advantageous current density is from 2.4 to 4.8 amp/dm². The period of treatment will then normally be from 4 to 15 minutes, e.g., from 7 to 10 minutes. However, there may be considerable departure from these conditions and the concentration of CrO_3 is at least 25 g/l, preferably from 250

to 850 g/l, and that of sulfuric acid is broadly 0.1 to 100 g/l, preferably from 1 to 10 g/l, while the temperature may vary from 10° C. to about 100° C., e.g., from 20° to 80° C., and the current density may be in the range 0.3 to 30 amp/dm², preferably 0.6 to 10 amp/dm², e.g., from about 1 to 5 amp/dm². In accordance with the variations in these factors, the duration of the treatment may then be as short as one-half minute, e.g., 2 minutes, or as long as 30 minutes. As those skilled in the art will appreciate, electrolysis of chromic acid aqueous solutions usually results in build up of trivalent chromium in the solution. Because the presence of trivalent chromium tends to limit the conditions under which deposition of bright layers of chromium will occur, the presence of trivalent chromium in amounts of 5 g/l or more in the chromic acid hardening baths used in the process of the present invention can be advantageous.

While the cathodic treatment is usually effected in the aqueous solution of chromic and sulfuric acid, it can also be carried out in solutions of chromic acid containing additions of silico-fluoride or fluoride ions added as the potassium salts either singly or in combination with sulfate ions. These solutions are not, however, as effective as the chromic/sulfuric acid solution since they show a much greater tendency to deposit chromium metal onto the surface of the steel. The hardening may also be effected in a solution of a trivalent chromium salt from which chromium can normally be plated, for example, trivalent chromium chloride hexahydrate dissolved in di-methyl formamide solution at a concentration of about 250 g/l.

As disclosed in U.K. Provisional Application No. 51164/71, filed in the United Kingdom on Nov. 3, 1971 (which application names A.N. Skedgell and V.A. Smith as inventors), the cathodic treatment may also be carried out in electrolytes containing about 0.25 to about 7.5 moles per liter of CrO_3, about 0.01 to about 1.0 mole per liter of H_2SO_4 together with sodium and ammonium ions adequate to bring the pH of the electrolyte into the range of 3 to 7.5.

Care must be exercised during the treatment since chromium tends to deposit on edges and corners where the current density is high. This may be avoided by shielding such areas and if necessary by making the current density low.

The cathodic treatment serves to harden the film and also to reduce its susceptibility to finger marking and staining. It is preferable to apply the hardening treatment as soon as possible after the coloring treatment in order to avoid the possibility of staining or marking of the unhardened film. Delay in application of the hardening treatment does not, however, prevent it being carried out effectively.

Both the coloring and hardening treatments can be carried out in lead-lined tanks heated by steam jackets, of the type used for conventional chromium plating. It is desirable to stir the coloring solution gently so as to maintain uniformity of temperature throughout it, but not to agitate either solution.

The resistance to corrosion can be tested by the CASS test described in BS 4601/1970, Appendix G, and various test panels have been subjected to this test.

In the first set of tests (Test 1) panels of 18/8 chromium-nickel austenitic stainless steel polished to a mirror finish were immersed in the optimum coloring solution, some for about 5 minutes to form uncolored films leaving the natural color of the steel, some for about 8 minutes to form blue films and some for about 10 minutes to form gold films. Some of the panels thus treated were put aside for the CASS test, and others were subjected to the cathodic hardening treatment at a cathodic current density of about 2.0 amp/dm² in an electrolyte containing 250 g/l CrO_3 and 2.5 g/l sulfuric acid at a temperature of 40° C. In another series of tests (Test 2) similar panels were treated in the same way except that only films of natural and blue color were produced. The results of CASS tests on all these panels and on untreated panels of the same steel in each case are shown in Table I.

TABLE I

Test	Treatment	Color	Result
1	Untreated	Natural	Moderately stained
	Uncolored	Natural	Moderately stained
	Colored	Blue	Heavily stained
	Colored	Gold	Heavily stained
	Uncolored and hardened	Natural	Very lightly stained
	Colored and hardened	Blue	Lightly stained
	Colored and hardened	Gold	Lightly stained
2	Untreated	Natural	Lightly stained
	Uncolored	Natural	Light/moderately stained
	Colored	Blue	Moderate/heavily stained
	Uncolored and hardened	Natural	Unstained
	Colored and hardened	Blue	Unstained

It will be seen that the resistance to staining of the panels subjected to the hardening treatment was distinctly better than that of those bearing unhardened films.

In other tests panels of mirror finish 17 percent chromium ferritic steel were similarly treated to produce uncolored and blue films and similarly tested with the results shown in Table II.

TABLE II

Treatment	Color	Result
Untreated	Natural	Moderate/light staining
Uncolored	Natural	Moderate staining
Colored	Blue	Moderate/heavy staining
Uncolored and hardened	Natural	Moderate/light staining
Colored and hardened	Blue	Moderate/light staining

The improvement in the abrasion resistance of colored films produced by means of the invention is shown by the results of tests in which panels bearing colored films are rubbed with a pencil eraser containing abrasive particles under a load of 500 g. and the number of rubs required to remove the coloring is noted.

Panels of an 18/8 chromium-nickel stainless steel polished to a mirror finish were colored blue by immersion in an aqueous solution containing 300 g/l of CrO_3 and 550 g/l of sulfuric acid at 70° C. for 8 minutes. The blue films thus formed were removed from some of these after from two to four rubs. The other panels were then given cathodic hardening treatment in aqueous solutions containing various amounts of chromic acid under various conditions of temperature, time of exposure and current density. The color of the test panels was virtually unaffected by this treatment. The colored and hardened panels were then rubbed, the tests being stopped after 200 rubs. The results are shown in Table III below in which "200+" means that the coating had not failed at this stage.

TABLE III

Solution composition	Cathodic Treatment Temp. °C.	Time Min-	Current Density amps/dm²	Rubs to failure
250 g/l CrO_3 + 2.5 g/l H_2SO_4	40	20	0.3	50
	40	20	0.6	160
	40	10	1.2	160
	40	20	1.2	200
	40	10	2.4	180
	40	15	2.4	200+
	40	20	2.4	200
	40	4	4.8	200+
	40	7	4.8	200+
	40	10	4.8	200+
	40	12	4.8	180
	40	15	4.8	100
	40	4	7.2	160
	40	10	7.2	160
	40	4	9.6	140
	40	6	9.6	130
	40	2	9.6	180
	40	2	14.4	120
	40	1	28.8	90
250 g/l CrO_3 + 2.5 g/l H_2SO_4	20	20	2.4	140
	20	10	4.8	80
	60	20	2.4	100
	60	10	4.8	40
	80	20	2.4	160
	80	10	4.8	50
25 g/l CrO_3 + 2.5 g/l H_2SO_4	40	20	2.4	120
	40	7	4.8	140
	40	10	4.8	60
100 g/l CrO_3 + 2.5 g/l H_2SO_4	40	10	2.4	40
	40	20	2.4	105
	40	7	4.8	120
	40	10	4.8	70
400 g/l CrO_3 + 2.5 g/l H_2SO_4	40	10	2.4	160
	40	20	2.4	180
	40	7	4.8	180
	40	10	4.8	200+
500 g/l CrO_3 + 2.5 g/l H_2SO_4	40	10	2.4	80
	40	20	2.4	90
	40	7	4.8	180
	40	10	4.8	120
750 g/l CrO_3 + 2.5 g/l H_2SO_4	40	10	2.4	180
	40	20	2.4	140
	40	7	4.8	120
	40	10	4.8	80
250 g/l CrO_3 + 10 g/l H_2SO_4	40	20	2.4	60
	40	10	4.8	70
250 g/l CrO_3 + 100 g/l H_2SO_4	40	20	2.4	60
	40	10	4.8	60

In further tests, mirror finished panels of three ferritic stainless steels were treated, namely 17 percent chromium, 13 percent chromium, and 17 percent chromium-1 percent molybdenum, steels respectively. The panels were all treated to develop a blue color, and this was removed from some after less than 6 rubs in each case. The remaining panels were cathodically treated in an electrolyte containing 250 g/l CrO_3 and 2.5 g/l H_2SO_4 at 40° C. for 20 minutes at a current density of 2.4 amp/dm², and these maintained the color for from 80 to 160 rubs.

It will be seen that the resistance of the coating to abrasion was substantially improved by each of the cathodic treatments.

In carrying out the invention, mechanically abraded steel surfaces preferably are employed to obtain an even color.

Corrosion resistant, chromium-containing alloys other than steel on which films can be formed and then satisfactorily cathodically hardened usually contain at least about 12.5 percent by weight of chromium and include iron-based nickel-chromium-molybdenum alloys such as an alloy containing 37 percent nickel, 18 percent chromium, 5 percent molybdenum, 1.2 percent titanium and 1.2 percent aluminum; cobalt-based alloys such as that containing 21 percent chromium, 21 percent nickel and 13 percent molybdenum; and nickel-chromium alloys, such as an alloy containing 30 percent chromium and 1 percent titanium, the remainder being nickel. For purposes of this specification and claims, stainless steels include iron-base alloys containing greater than about 11 percent and up to about 30 percent chromium. The oxidic layers which are hardened in accordance with the present invention are very thin, i.e, of a thickness up to and including the thicknesses of layers exhibiting optical interference effects. Thus, as indicated hereinbefore, the films which are formed by wet oxidation on the surface of chromium-containing metal using immersion or electrolytic techniques can be colorless or can be of any color, including black, which is generated by optical interference and/or absorption.

It is possible to produce different colors on different areas of the alloy surface by forming an acid-resisting layer on one or more areas, initiating the film-forming treatment so as to form a film on the other area or areas, removing the acid-resisting layer or layers, completing the coloring treatment, and then subjecting the whole alloy to the cathodic hardening treatment.

Mechanical deformation does not appear to detrimentally affect the hardened coating or film, and the treated material can be bent, deep drawn and rigidized without cracking the film or reducing the color intensity of the deformed areas. In demonstrating this, the colored and hardened material has been bent through 90° without cracking or flaking the colored films or reducing the color intensity at the bent portion. Further, the material has been deep drawn to form a cup 35 mm. in diameter by 20 mm. deep without damaging the colored film. Colored and hardened panels have also been rigidized, by deforming them in a diamond pattern without cracking the film or reducing its color intensity. Another advantage of stainless steel treated in accordance with the invention is that the hardened colored films resist boiling water well so it is possible to produce kitchen utensils such as saucepans of stainless steel in attractive colors which are not rapidly lost in use.

It has also been found that treatment of the coated steel by the process of the invention renders it less retentive of finger marks caused by greasy deposits from the skin. It is presently believed that the cathodic treatment renders the coating less porous and thus less absorbent to these greasy deposits and the process may also usefully be applied to stainless steel bearing other porous coatings that are not themselves attacked and removed by the acid solution.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A process for treating metal containing at least about 11 percent by weight of chromium comprising initially treating the surface of said metal in an aqueous, acidic oxidizing bath to form thereon a thin oxidic coating having a thickness up to and including thicknesses which exhibit optical interference effects, said oxidic coating being deficient in abrasion resistance and thereafter treating the coated metal electrolytically as a cathode in a bath from which chromium can be de-

posited for at least about 1 minute under conditions of temperature and cathodic current density adequate to harden the coating but insufficient to produce a visible, white deposit of chromium on said metal surface or otherwise affect the color of the coated surface whereby the surface of said chromium-containing metal is rendered more corrosion and abrasion resistant.

2. A process according to claim **1** wherein the corrosion-resistant, chromium-containing metal is a stainless steel.

3. A process according to claim **2** wherein the stainless steel is initially treated to form a colored, immersion coating.

4. The process of claim **1** wherein the initial treatment comprises immersion of the surface in an aqueous solution containing about 200 to about 400 g/l chromic acid, about 350 to about 700 g/l sulfuric acid, at a temperature of about 65° to about 80° C. for a time of at least about 5 minutes.

5. A process according to claim **4** wherein said immersion treatment is conducted for a time sufficient to produce at least a blue color on said stainless steel.

6. A process according to claim **5** wherein said aqueous solution contains about 300 g/l chromic acid, about 550 g/l sulfuric acid and is used at a temperature of about 70° C.

7. The process of claim **1** wherein the initial treatment is conducted in an aqueous solution of chromic acid.

8. A process according to claim **1** wherein the immersion coating is produced in an aqueous solution containing 50 to 1,000 g/l chromic acid, up to 600 g/l sulfuric acid and up to 50 g/l manganous sulfate.

9. A corrosion-resistant, metal containing at least about 11 percent chromium and having a thin, oxidic coating on at least part of the surface thereof of a thickness up to thicknesses exhibiting optical interference effects, said coating having been produced by treatment in an aqueous acidic solution and said coating having been electrolytically treated for at least about one minute as a cathode in a bath from which chromium can be deposited under conditions of time, temperature and cathodic current density adequate to harden said coating but insufficient to produce a visible, white deposit of chromium on said coated surface or otherwise affect the color of the coated surface.

* * * * *