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[54] **ELECTROLYTIC TREATMENT OF STAINLESS STEEL HAVING AN OXIDIC FILM**

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[56] **References Cited**

UNITED STATES PATENTS

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[57] **ABSTRACT**

Oxidic films on stainless steel and similar alloys formed by treatment of the alloys in aqueous solutions of sulfuric acid and pitting inhibiting oxidizing agents, are hardened by being treated as cathodes in aqueous electrolytes containing metal ion having a pH in excess of about 0.5 and within the range for the particular metal of the solution whereby oxide will form at the cathode rather than metal.

9 Claims, No Drawings

ELECTROLYTIC TREATMENT OF STAINLESS STEEL HAVING AN OXIDIC FILM

The present invention is concerned with hardening oxidic films formed on iron-base, chromium-containing, corrosion-resistant alloys, e.g., stainless steels, by treatment of said alloys in aqueous sulfuric acid solutions containing a pitting inhibiting oxidizing agent(advantageously chromic acid).

A known method of treating stainless steel and other chromium-containing alloys comprises two main steps, in the first of which an oxidic film is formed on the surface of the alloy by immersion of the alloy in an aqueous solution of chromic and sulfuric acids, with or without other constituents, and in the second of which the alloy bearing the film is subjected to electrolysis as the cathode in an electrolyte from which chromium can be deposited. This method is the subject of U.S. applications Ser. Nos. 114,357 and 252,459, filed in the name of Anthony C. Hart, in which it is explained that the electrolytic treatment is short, lasting for a period of time adequate to harden the film, but not so long that any chromium becomes visible on the surface as a white deposit.

In practice of the Hart process, there is an increasing tendency for chromium metal to be deposited from aqueous electrolytes containing chromic and sulfuric acids as the current density increases, and, at the comparatively low current density required to ensure that no chromium metal is deposited, it is difficult to harden the film completely. Our object in the present invention is to eliminate or at least to reduce this disadvantage.

We have found that the acidity of the electrolyte plays an important part in the hardening step, and that above a certain pH value in an electrolyte containing hexavalent chromium ions, no chromium metal is deposited. We have also found using aqueous solutions of metal ion as electrolytes that above about a pH of 0.5 and within a restricted range of pH particular to each metal of the group set forth hereinafter, metal oxidic species will be deposited preferentially at a cathode and that these aqueous solutions of metal ions can be used as electrolytes in the electrolysis process to harden films on stainless steel in a manner similar to the use of aqueous solutions containing hexavalent chromium.

It is an object of the invention to provide a novel process for hardening oxidic films on stainless steel and similar alloys.

Another object of the present invention is to provide an advantageous electrolyte useful for hardening oxidic films on stainless steel and similar alloys.

Generally speaking, the present invention contemplates a process for hardening an oxidic film produced on an iron-base, chromium-containing, corrosion-resistant alloy by treatment in an aqueous sulfuric acid bath containing a pitting inhibiting oxidizing agent comprising treating as the cathode the surface of such an alloy bearing such an oxidic film in an aqueous solution of metal from the group of aluminum, titanium, vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, tin and silicon, said aqueous solution having a pH in excess of about 0.5 and within a specially selected range particular as to each metal-bearing ion so as to deposit at the cathode surface metal oxide, hydrated oxide or hydroxide

in preference to metal and thereby increase the resistance of said oxide film to abrasion.

Generally speaking, if the pH of the solutions is too low, metal oxide will not be formed at the cathode, whereas if the pH of the solution is too high, the metal-bearing ion will sometimes tend to hydrolyze in the bulk of the solution to form an oxidic precipitate.

According to one aspect of the invention, the composition of an electrolyte containing hexavalent chromium ions is formulated such as to bring the pH into the range in which chromium metal is not deposited. This can be done by the addition of sodium hydroxide or ammonium hydroxide to a chromic acid electrolyte.

Generally speaking, this aspect of the process of the present invention comprises cathodically treating the surface of an iron-base, chromium-containing, corrosion-resistant alloy bearing an oxidic film produced by treatment in an aqueous sulfuric acid bath containing a pitting inhibiting oxidizing agent in an aqueous electrolyte containing about 25 grams per liter (gpl) to about 750 gpl of hexavalent chromium specie measured as CrO_3, and a hydroxide, carbonate or the like from the group consisting of ammonium, potassium and sodium hydroxide and carbonate in an amount sufficient to at least partly neutralize the chromium-containing anions and sufficient to maintain the bulk pH of the electrolyte in the range of about 3 to about 7.5. The cathodic treatment is carried out at a cathode current density of about 2 to about 40 amperes per square decimeter (A/dm^2) for about 2 to about 40 minutes while the electrolyte is held at a temperature of about 20°C. to about 60°C. Advantageously, the electrolyte contains at least about 100 gpl of chromic acid (measured as CrO_3). A particularly useful standard electrolyte contains about 2.5 moles of CrO_3 (250 grams) per liter and sufficient NaOH or NH_4OH (about 3.5 to 5.2 moles of NaOH) to bring the pH of the electrolyte to about 6.3 to about 7.5. Advantageously, the cathode current density during hardening is within the range of about 8 to about 12 A/dm^2.

The initial film formed by immersion of stainless steel in chromic and sulfuric acids probably consists of a hydrated iron and chromium-rich, spinel-type oxide and it seems that the hardening result from the entry of Cr_2O_3 into the pores of this film. Chromium metal may also be deposited on the surface and if this happens it spoils the appearance of the film. Rendering the electrolyte less acidic appears to promote electrolytic conditions within the film which favor deposition of Cr_2O_3 into the pores. However, this may be in a hardening electrolyte consisting of 2.5 molar (M) CrO_3 and 0.01M $(NH_4)_2S_2O_8$ and operated at a current density of about 10.8 A/dm^2 chromium metal is deposited and only a moderate amount of hardness is achieved. When NaOH is progressively added to the electrolyte, chromium metal continues to be deposited until the molar ratio NaOH: CrO_3 exceeds 0.8. When the molar ratio is within the range 0.4 to 2.1, there is a striking increase in the hardness of the film. When the molar ratio exceeds 2.1, a surface deposit of $Cr(OH)_3$ is formed which becomes visible if the cathodic charge is high, that is to say, above about 5.4×10^4 coulombs per square decimeter. The surface deposit of chromium hydroxide prevents entry of Cr_2O_3 into the film, with catastrophic effects on its hardness. In an electrolyte containing 2.5M CrO_3, therefore, the molar ratio is prefer-

ably adjusted within the range 1.4 to 2.1 to yield pH within the range 6.3 to 7.5 by the addition of from 3,5M to 5.2M NaOH.

Typical conditions for the hardening of blue films formed on 18/8 stainless steel are a cathodic current density of 10.8 A/dm^2 for about 15 minutes while the electrolyte is at a temperature of about 40°C.

This aspect of the invention includes hexavalent chromium-containing electrolytes in which the hardening can be effected, these containing the reaction products of from 0.25M to 7.5M CrO_3, together with basic ions, e.g., sodium or ammonium ions, adequate to bring the pH into the range of 3 to 7.5. Such an electrolyte can be made by adding chromic acid to a solution of sodium chromate or ammonium chromate, or by adding sodium or ammonium hydroxide to a solution of chromic acid.

The invention presents the three advantages of increasing the hardness of the films, avoiding the deposition of chromium metal and enabling the current density to be increased during the hardening process.

In order to give those skilled in the art a better understanding and appreciation of this apsect of the invention, the following examples are given.

EXAMPLES

A series of aqueous hardening baths were set up having compositions in moles per liter (m/l) as set forth in Table I. Baths designated by letters are outside the ambit of the present invention, whereas those marked by numbers are examples of baths within the ambit of the present invention.

TABLE I

Bath Designation	CrO_3 (m/l)	$(NH_4)_2SO_2O_8$ (m/l)	NaOH (m/l)	Current Density (A/dm^2)	pH
A	2.5	0.01	0	9.7	*
B	2.5	0.01	1	11.6	*
C	2.5	0.01	2	11.2	−0.025
1	2.5	0.01	3	15.9	6.06
2	2.5	0.01	4	11.6	6.65
3	2.5	0.01	5	14.3	7.22
D	2.5	0.01	6	12.0	13.60

*indeterminate, negative pH value

Type 304 stainless steel panels were treated in an aqueous solution containing chromic acid and sulfuric acid to produce on the surface thereof an oxidic film having a blue color. An arbitrary test for abrasion resistance comprising rubbing with a green rubber eraser was set up and it was found that this blue colored film was removable with only one or two rubs. The panels were than hardened in the baths set froth in Table I by treating them cathodically at the cathodic current densities indicating in Table I for 15 minutes with the results being obtained as set forth in Table II.

TABLE II

Bath Designation	Rubs for Film Removal (average of 3 trials)	Over Film Deposit (if any)
A	35	Cr metal
B	50	Cr metal
C	55	Cr metal
1	60	—
2	65	—
3	80	—
D	25	$Cr(OH)_3$

Tables I and II show that when the pH of a hardening solution containing hexavalent chromium is between 3 and 7.5 advantageous improvements of abrasion resistnace of oxidic films can be obtained at high cathodic current densities without the risk of metallic chromium deposition. Above pH 7.5 no effective hardening is obtained and below pH 3, metallic chromium forms on the surface at high cathode current densities.

It has also been found that oxides other than chromium can be utilized for hardening the film. To this end the metal carrying the coating or colored film to be hardened is immersed in an aqueous solution of salts of, for example, aluminum, titanium, vanadium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, tin and silicon and made the cathode in the solution. Subsequently, cathodic electrolysis is carried out until the film is hardened.

The selection of a suitable hardening solution employing a metal salt entails the choice of a salt of a metal which has an oxide insoluble in water and which preferably forms a neutral or slightly acidic solution. Either the solution of such a salt must be capable of depositing the oxide if the pH value of the solution is raised, or it must form an oxide by cathodic reduction of a soluble species in the solution, or it must form an oxide by a combination of both these effects. The color of the oxide deposited has little or no effect on the color of the film, although the color of the film is usually slightly advanced in shade.

Examples of mirror finish Type 304 stainless steel plate given a blue film coating by immersion in a chromic and sulfuric acids solution, and hardened by cathodic electrolysis in an electrolyte according to the invention will now be described. In these examples, the experimental variables, apart from the solution, include current density, time of process, pH value and temperature, and the effects of the hardening treatment are to harden the film and slightly to advance the color of the film in shade. Undesirable effects during hardening are metal deposition, oxide deposition on top of the film and too great or uneven color advancement. Hardness of the film is measured in the examples by a "standard rub-test" which consists of rubbing the film surface with a pencil-type eraser, preferably Remington, loaded with a 400 gram weight. For example, an unhardened film would fail in one or two rubs whereas a film hardened according to the invention may withstand 100 to 150 rubs or more before failure.

EXAMPLE 4

Potassium permanganate in an aqueous solution was employed as the hardening electrolyte. The hardening mechanism makes use of the fact that Mn^{VII} in the form of the MnO_4^- anion is stable in solution in the neutral-alkaline pH range. It is though that when MnO_4^- is reduced at the cathode sites, i.e., within the pores of the color-film, Mn^{IV} is produced and precipitated as the insoluble MnO_2, possibly hydrated. Test conditions were 0.4M $KMnO_4$ (63 gpl) solution, pH 8.5 at room temperature. Results of the tests are set forth in Table III.

TABLE III

Current Density (A/dm^2)	Time (in sec.)	Hardness (no. of rubs to failure)	Remarks
0.05	30	30	Slight color advancement to late (pale) blue

TABLE III-Continued

Current Density (A/dm^2)	Time (in sec.)	Hardness (no. of rubs to failure)	Remarks
0.05	60	30	Moderate color advancement to early (pale) gold
0.2	20	20	Moderate color advancement to gold/red
0.2	60	30	Severe color advancement to blue/green

Conclusions to be drawn from the data set forth in Table III and other observations are that use of cathodic treatment in potassium permanganate solution results in (a) moderate hardening increase; (b) improved resistance to finger marking; and (c) considerable color advancement.

EXAMPLE 5

Nickel nitrate in an aqueous solution was employed as the hardening electrolyte. It is thought that unlike the $KMnO_4$ or CrO_3 hardening process no electrochemical reduction of metal ion species takes place. The main reduction at the cathode is hydrogen ion discharge, $H^+ + e^- \rightarrow \frac{1}{2} H_2$. This causes the pH values within the pores of the color film to rise, the solubility product of the metal-hydroxide is exceeded and nickel hydroxide is precipitated within the pores. 0.5M (91 gpl) $Ni(NO_3)_2$ was used. Results of tests using nickel nitrate as the electrolyte are set forth in Table IV.

TABLE IV

Current Density (A/dm^2)	Time (in sec.)	pH	Hardness (no. of rubs to failure)	Remarks
0.5	60	6.7	—	$Ni(OH)_2$ deposition within pores as shown by slight color advancement. Also some $Ni(OH)_2$ deposited on top of color film
0.2	20	6.7	40	$Ni(OH)_2$ deposition only within pores of color film. Slight color advancement
0.4	15	6.7	80	Slight color advancement. $Ni(OH)_2$ deposition only wihtin pores of film
0.8	5	6.7	40	Slight color advancement. $Ni(OH)_2$ deposition only within pores of film

The last three experiments in Table IV were repeated using $Ni(NO_3)_2$ solutions with pH values adjusted to 5.7 and 4.7 with very similar results. Raising the temperature to 40°C. and 60°C. did not cause any further improvement.

The data in Table IV shows that reasonable hardening is possible in $Ni(NO_3)_2$ solutions. As long as the current and time are restricted as shown in Table IV, there are no problems of changes in appearance of the specimens.

EXAMPLE 6

Zinc nitrate in an aqueous solution was employed as the hardening electrolyte. It is thought that the hardening mechanism is the same as for the $Ni(NO_3)_2$ process of Example 5. Test conditions were 0.5M (95 gpl) $Zn(NO_3)_2$ at room temperature. Results are set forth in Table V.

TABLE V

Current Density (A/dm^2)	Time (in sec.)	pH	Hardness (no. of rubs to failure)	Remarks
0.4	15	3.7	—	$Zn(OH)_2$ deposition within pores as shown by slight color advancement. Also some $Zn(OH)_2$ deposited on top of color film
0.2	15	3.7	40	$Zn(OH)_2$ deposition only within pores of color film. Slight color advancement
1.0	30	1.5	20	Slight color advancement. $Zn(OH)_2$ deposited only within pores of color film.
2.0	30	1.5	—	$Zn(OH)_2$ deposition in pores and on top of color film

The $Zn(NO_3)_2$ solution gave some hardening although the results were not as good as in the $Ni(NO_3)_2$ solution of Example 5. It appears necessary for the current and time to be reduced to avoid loose oxide/hydroxide deposit on top of the color film and this limits the degree of hardening that can be achieved. Reducing the pH to 1.5 shifted the acceptable current density and time to higher levels, but no increase in hardness resulted.

EXAMPLE 7

Aluminum sulfate in an aqueous solution was employed as the hardening electrolyte. It is thought that the hardening mechanism is the same as for Examples 5 and 6. Test conditions were 0.5M (171 gpl) $Al_2(SO_4)_3$ at room temperature. Results are set forth in Table VI.

TABLE VI

Current Density (A/dm^2)	Time (in sec.)	pH	Hardness (no. of rubs to failure)	Remarks
0.4	60	2	20	Slight color advancement
4.0	15	2	100	Moderate color advancement, particularly around edges
4.0	15	1	80	Moderate color advancement, particularly around edges

The data in Table VI show that in $Al_2(SO_4)_3$ solutions it is possible to get reasonably good hardening without too much color advancement or oxide deposition on top of the color film.

When employed in this specification and claims, the term "iron-base, corrosion-resistant, chromium-containing alloy" includes stainless steels and other iron-containing alloys which also contain greater than about 11 percent and up to about 30 percent by weight of chromium. Stainless steels can be ferritic or austenitic and usually contain about 13 percent to about 25 percent (by weight) chromium.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be re-

sorted 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.

We claim:

1. A process for hardening an oxidic film on iron-base, chromium-containing, corrosion-resistant alloy formed by treatment of said alloy in an aqueous solution of sulfuric acid and chromic acid which process comprises treating said alloy having said film on the surface thereof as a cathode in an aqueous solution having a pH in excess of about 0.5, containing in ionic form metal from the group consisting of aluminum, titanium, vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, tin and silicon and having the pH regulated within a special range for each type of ion so that oxide will be deposited at said cathodic surface in preference to metal.

2. A process as in claim **1** wherein the iron-base, chromium-containing, corrosion-resistant alloy is stainless steel.

3. A process as in claim **2** wherein the aqueous solution contains about 0.25 to about 7.5 moles per liter of CrO_3, and sufficient base to maintain the pH of the solution in the range of about 3 to about 7.5.

4. A process as in claim **3** wherein the aqueous solution has a pH of about 6.3 to about 7.5.

5. A process as in claim **1** wherein the metal ion in aqueous solution is hexavalent chromium and the pH is in the range of about 3 to about 7.5.

6. A process as in claim **1** wherein the metal ion in aqueous solution is trivalent aluminum.

7. A process as in claim **1** wherein the metal ion in solution is heptavalent manganese.

8. A process as in claim **1** wherein the metal ion in solution is divalent nickel.

9. A process as in claim **1** wherein the metal ion in solution is divalent zinc.

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