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(54) ELECTROLYTIC TREATMENT OF CHROMIUM-CONTAINING ALLOYS AND ELECTROLYTES FOR USE THEREIN

(71) We, INTERNATIONAL NICKEL LIMITED, a British Company, of Thames House, Millbank, London S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion-resistant chromium-containing iron alloys, and is particularly applicable to stainless steel.

A method has been proposed of improving the resistance to both corrosion and abrasion of stainless steel and other chromium-containing iron alloys on which a porous film has been formed by means of an aqueous solution of chromic and sulphuric acids with or without electrolysis, which comprises subjecting the alloy bearing the porous film to cathodic electrolysis in an electrolyte from which chromium can be deposited, 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. The hardening of the film was attributed to the deposition of metallic chromium in the pores of the film, and the use of an electrolyte from which chromium could be deposited was therefore regarded as essential.

It is a disadvantage of this process that only relatively low current densities can be used, since in practice there is an increasing tendency for chromium metal to be deposited on the surface of the film as the current density increases.

Surprisingly it has now been found that the film can be hardened by the formation in pores of the film of an oxidic deposit rather than metallic chromium, so that other electrolytes can be used for hardening.

According to the invention the hardness of a porous film formed on the surface of a corrosion-resistant chromium-containing iron alloy by treatment of the alloy in an aqueous solution of chromic and sulphuric acids, with or without other constituents, is increased by

subjecting the alloy bearing the porous film to electrolysis as the cathode in a hardening electrolyte from which an oxidic deposit is formed in the film pores as a result of cathodic reduction of ions derived from a soluble salt containing a metallic element in the electrolyte and/or a rise in pH within the film pores brought about by the electrolysis, the cathodic electrolysis and thereby the formation of the oxidic deposit being carried out for a period of time sufficient to harden the film but not long enough for the oxidic deposit to be formed on the film surface, and the composition of the hardening electrolyte and the current density being such that the metallic element would not be deposited on prolonging the electrolysis. The oxidic deposit may consist of an insoluble oxide, hydroxide or hydrated oxide. The hardening electrolyte may or may not contain chromium. When a chromium-containing electrolyte is used we find that the acidity of the electrolyte plays an important part in the hardening step, and that above a certain pH value, no chromium metal is deposited.

In one way of carrying out the invention the composition of a chromium containing hardening electrolyte is made such as to bring the pH into the range in which chromium metal is not deposited. This may be done by the addition of a suitable base.

The hardening electrolyte is suitably an aqueous electrolyte containing from 25 to 750 g/l (grams per litre) of hexavalent chromium, measured as CrO_3 , and an added base in an amount sufficient to at least partly neutralise the chromium-containing anions and sufficient to maintain the bulk pH of the electrolyte in the range of 3 to 7.5. The cathodic treatment may be carried out at a cathode current density of from 2 to 40 amperes per square decimetre (A/dm^2) for 2 to 40 minutes while the electrolyte is held at a temperature of from 20 to 60°C. The added base may be sodium, potassium or ammonium hydroxide or carbonate.

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Advantageously, the electrolyte contains at least 100 g/l of chromic acid (measured as CrO_3). A particularly useful electrolyte contains about 2.5 moles of CrO_3 (250 grams) per litre, and 3.5 to 5.2 moles per litre of sodium, potassium or ammonium hydroxide or carbonate, preferably NaOH or NH_4OH , to bring the pH of the electrolyte to 6.3 to 7.5. Advantageously, the cathode current density during hardening with the foregoing electrolyte is within the range of 8 to 12 A/dm^2 .

The initial film formed on stainless steel in chromic and sulphuric acids consists of a hydrated iron and chromium-rich, spinel-type oxide and the hardening in a chromium-containing hardening electrolyte results from the entry of an oxidic deposit, particularly Cr_2O_3 , into the pores of this film. Rendering the electrolyte less acidic appears to promote electrolytic conditions within the film which favour the deposition of Cr_2O_3 into the pores, while avoiding the formation of a metallic chromium deposit on the surface. From a hardening electrolyte consisting of 2.5M CrO_3 and 0.01M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and operated at a current density of about 10.8 A/dm^2 for 15 minutes chromium metal is deposited on the surface and only a moderate amount of hardening is achieved. When NaOH is progressively added to the electrolyte chromium metal continues to be deposited on the surface on prolonged electrolysis until the molar ratio $\text{NaOH}:\text{CrO}_3$ exceeds 0.8:1. When the molar ratio $\text{NaOH}:\text{CrO}_3$ is within the range 1.4:1 to 2.1 there is a striking

increase in the hardness of the film. When the molar ratio $\text{NaOH}:\text{GO}_3$ exceeds 2.1:1 a surface deposit of $\text{Cr}(\text{OH})_3$ is formed which becomes visible if the cathodic charge is high, that is to say above 5.4×10^4 coulombs per square decimetre. The surface deposit of chromium hydroxide prevents entry of Cr_2O_3 into the film, with catastrophic effects on its hardness. In a hardening electrolyte containing 2.5M CrO_3 , therefore, the molar ratio $\text{NaOH}:\text{CrO}_3$ is adjusted within the range 1.4:1 to 2.1:1 to yield pH within the range 6.3 to 7.5 by the addition of from 3.5M to 5.2M NaOH .

EXAMPLE 1.

Table 1 shows the degree of hardening achieved in a series of tests in which Type 304 (18 to 20% chromium, 8 to 12% nickel) stainless steel, previously coloured blue by immersion in a chromic and sulphuric acid solution, was cathodically treated in hardening electrolytes containing 2.5M $\text{CrO}_3 + 0.01\text{M } (\text{NH}_4)_2\text{S}_2\text{O}_8$ at 40°C to which varying amounts of NaOH were added to influence the pH of the solution in the manner described above. In each of the tests in Table 1, the hardness of the film was determined by a rub test which consisted in rubbing the surface of the film with an ink eraser, the number of rubs to failure of the films being a measure of the hardness. A, B, C and D in Table 1 are outside the invention whilst tests 1A, 1B and 1C in Table 1 are according to the invention.

TABLE 1

Tests	Additions of $\text{NaOH}(\text{M})$	pH	Current Density A/dm^2	Time in mins	Hardness (No. of rubs to failure)	Remarks
A	—	*	9.7	15	35	Metallic Cr on film surface
B	1	*	11.6	15	50	Metallic Cr on film surface
C	2	-0.025	11.2	15	55	Metallic Cr on film surface
1A	3	6.06	15.9	15	60	$\text{Cr}(\text{OH})_3$ on film surface
1B	4	6.65	11.6	15	65	
1C	5	7.22	14.3	15	80	
D	6	13.60	12.0	15	25	

* indeterminate negative pH value.

It can be seen from the data set forth in Table 1 that treatment at 40°C in hardening electrolytes containing 2.5M CrO₃+0.01M (NH₄)₂S₂O₈ was most effective with NaOH additions of from 3M to 5M to give pH values in the range of 6.06 to 7.22 and with current densities ranging from 11.6 to 15.9 A/dm² for 15 minutes, yielding moderate hardening. If the pH of the hardening electrolyte is too low, metallic chromium deposits on the film, whereas if the pH of the hardening electrolyte is too high the chromium-bearing ion tends to hydrolyse in the bulk of the hardening electrolyte to form a precipitate of Cr(OH)₃ on the film surface.

The invention includes electrolytes in which the hardening can be effected, containing from 0.25M to 7.5M CrO₃ together with sufficient base, e.g. one or more of sodium hydroxide, potassium hydroxide, or ammonium hydroxide, 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, potassium chromate or ammonium chromate, or by adding sodium hydroxide or carbonate, potassium hydroxide or carbonate or ammonium hydroxide or carbonate to a solution of chromic acid.

It has also been found that oxides other than chromium oxide can be utilised for hardening the film, and in another way of carrying out the invention the metal carrying the porous coating or coloured film to be hardened is made the cathode in an aqueous solution of a salt of an element that forms an oxide insoluble in water. Subsequently cathodic electrolysis is carried out to deposit the oxide in the pores of the film until the film is hardened.

Suitable hardening solutions are those which contain a salt of an element which has an oxide insoluble in water and which is capable either of depositing the oxide if the pH value of the solution is raised, or of forming an oxide by cathodic reduction of a soluble species in the solution, or of forming an oxide by a combination of both these effects. Suitable oxides are formed by elements such as Al, Ti, V, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Sn and Si. The colour of

the oxidic deposit has little or no effect on the colour of the film, although the colour of the film is usually slightly advanced in shade, in the colour series brown, blue, gold, magenta, peacock and green.

Some examples of the hardening of blue coatings formed on mirror finish Type 304 stainless steel plate by immersion in a solution of chromic and sulphuric acids, by cathodic electrolysis in non-chromium-containing hardening electrolytes 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 colour of the film in shade. Undesirable effects are metal deposition, oxide deposition on top of the film and too great or uneven colour advancement. The hardness of the film was 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 400g weight. In this test an unhardened film would fail in one or two rubs, whereas a film hardened according to the invention may withstand up to 100 to 150 rubs before failure, and particularly satisfactory hardening treatments may give films that withstand as many as 400 to 600 rubs.

EXAMPLE 2.

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 MnO₄⁻ anion is stable in solution in the neutral-alkaline pH range. It is thought that when MnO₄⁻ is reduced at the cathode sites, i.e. within the pores of the colour-film, Mn^{IV} is produced and precipitated as the insoluble MnO₂, possibly hydrated. Test conditions were 0.4M KMnO₄ (63 g/l) solution, pH 8.5, at room temperature, and the Mn was present in the electrolyte as heptavalent manganese ions.

Table 2 shows the results obtained according to the invention.

TABLE 2

Current Density A/dm ²	Time (in seconds)	Hardness (No. of rubs to failure)	Remarks
0.05	30	30	Slight colour advancement to pale blue
0.05	60	30	Moderate colour advancement to pale gold
0.2	20	20	Moderate colour advancement to gold/red
0.2	60	30	Severe colour advancement to blue/green

It can be seen from the data set forth in Table 2, that treatment in KMnO_4 solutions yields a moderate increase in hardness and considerable colour advancement.

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EXAMPLE 3.

Nickel nitrate in an aqueous solution was employed as the hardening electrolyte. It is thought that unlike the KMnO_4 or CrO_3 hardening processes no electrochemical reduction of metal ion species takes place. The main reaction at the cathode is hydrogen ion

discharge $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$. This causes the pH values within the pores of the colour film to rise, so that the solubility product of the metal-hydroxide is exceeded and nickel hydroxide is precipitated within the pores. The hardening electrolyte used contained 0.5M (91 g/l) $\text{Ni}(\text{NO}_3)_2$, and the Ni was present in the electrolyte as divalent Ni ions.

Results of tests using nickel nitrate are set forth in Table 3, in which the test at 0.5 A/dm² is outside the invention and the other three tests are according to the invention.

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TABLE 3

Current Density A/dm ²	Time (in seconds)	pH	Hardness (No. of rubs to failure)	Remarks
0.5	60	6.7	—	$\text{Ni}(\text{OH})_2$ deposition within pores as shown by slight colour advancement, also some $\text{Ni}(\text{OH})_2$ deposited on top of colour film.
0.2	20	6.7	40	$\text{Ni}(\text{OH})_2$ deposition only within pores of colour film. Slight colour advancement.
0.4	15	6.7	80	$\text{Ni}(\text{OH})_2$ deposition only within pores of colour film. Slight colour advancement.
0.8	5	6.7	40	$\text{Ni}(\text{OH})_2$ deposition only within pores of colour film. Slight colour advancement

The last three experiments in Table 3 were repeated using $\text{Ni}(\text{NO}_3)_2$ 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.

It can be thus seen that reasonable hardening is possible in $\text{Ni}(\text{NO}_3)_2$ solutions, and provided that the current density and time are restricted to 0.2 to 0.8 A/dm² and to from 5 to 20 seconds as shown in Table 2 there are no problems of changes in appearance of the specimens. As shown by the first experiment in Table 3 too large current den-

sities for too long a time produce oxidic deposition on top of the film.

EXAMPLE 4.

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 $\text{Ni}(\text{NO}_3)_2$ process of Example 3. Test conditions were 0.5M (95 g/l) $\text{Zn}(\text{NO}_3)_2$ at room temperature. The Zn was present in the electrolyte as divalent Zn ions.

Table 4 shows the results obtained with the tests at 0.4 and 2.0 A/dm² being outside the invention; the other two tests being according to the invention.

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TABLE 4

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

It can thus be seen that the Zn(NO₃)₂ hardening electrolyte gave some hardening although the results were not as good as in the Ni(NO₃)₂ solution of Example 3. The current density must be low enough and the time short enough to avoid loose oxide/hydroxide deposit on top of the colour film and this limits the degree of hardening that can be achieved. Lowering the pH to 1.5 shifted the acceptable current density and time to higher levels but no increase in hardness resulted.

EXAMPLE 5.

Aluminium sulphate in an aqueous solution was employed as the hardening electrolyte. It is thought that the hardening mechanism is the same as for Examples 3 and 4. Test conditions were 0.5M (171 g/l) Al₂(SO₄)₃ at room temperature. The Al was present in the electrolyte as trivalent Al ions.

Table 5 shows the results obtained according to the invention.

TABLE 5

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

In $\text{Al}_2(\text{SO}_4)_3$ solutions it is possible to get reasonably good hardening without too much colour advancement or oxide deposition on top of the colour film.

5 WHAT WE CLAIM IS:—

1. A method of increasing the hardness of a porous film formed on the surface of a corrosion-resistant chromium-containing iron alloy by treatment of the alloy in an aqueous solution of chromic and sulphuric acids, with or without other constituents, in which the alloy bearing the porous film is subjected to electrolysis as the cathode in a hardening electrolyte from which an oxidic deposit is formed in the film pores as a result of cathodic reduction of ions derived from a soluble salt containing a metallic element in the electrolyte and/or a rise in pH within the film pores brought about by the electrolysis, the cathodic electrolysis and thereby the formation of the oxidic deposit being carried out for a period of time sufficient to harden the film but not long enough for the oxidic deposit to be formed on the film surface, and the composition of the hardening electrolyte and the current density being such that the metallic element would not be deposited on prolonging the electrolysis.

2. A method according to claim 1 in which the hardening electrolyte contains in ionic form in aqueous solution one or more of the elements aluminium, titanium, vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, silicon or tin.

3. A method according to claim 2 in which the element ion in the hardening electrolyte is hexavalent chromium and in which the pH value of the hardening electrolyte is in the range of 3 to 7.5.

4. A method according to claim 2 in which the element ion is trivalent aluminium.

5. A method according to claim 2 in which the element ion is heptavalent manganese.

6. A method according to claim 2 in which the element ion is divalent nickel.

7. A method according to claim 2 in which the element ion is divalent zinc.

8. A method according to claim 1 in which the hardening electrolyte is an aqueous solution containing 0.25 to 7.5 moles per litre of CrO_3 , and sufficient base to maintain the pH value of the solution in the range 3 to 7.5.

9. A method according to claim 8 in which the aqueous solution has a pH value of 6.3 to 7.5.

10. A method according to claim 9 in which the aqueous solution contains 2.5 moles per litre of CrO_3 and 3.5 to 5.2 moles per litre of a base from the group of sodium, potassium and ammonium hydroxides or carbonates.

11. A method according to any one of claims 1 to 10 in which the alloy is stainless steel.

12. A method of increasing the hardness of a porous film on a corrosion-resistant chromium-containing iron alloy as claimed in claim 1 and substantially as hereinbefore described with reference to Examples 1 to 5.

13. An electrolyte for cathodically hardening a porous film formed on the surface of a corrosion-resistant chromium-containing iron alloy by treatment of the alloy in an aqueous solution of chromic and sulphuric acids, with or without other constituents, said electrolyte comprising 0.25 to 7.5 moles per litre of CrO_3 , and sufficient base to provide a pH value in the range 3 to 7.5.

14. An electrolyte according to claim 13, wherein the pH is in the range 6.3 to 7.5.

15. An electrolyte according to claim 14, containing 2.5 moles per litre of CrO_3 and 3.5 to 5.2 moles per litre of a base from the group of sodium, potassium and ammonium hydroxides or carbonates.

16. A corrosion-resistant chromium-containing iron alloy article having on a surface thereof a porous film increased in hardness by the method according to claim 1.

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In $\text{Al}_2(\text{SO}_4)_3$ solutions it is possible to get reasonably good hardening without too much colour advancement or oxide deposition on top of the colour film.

5 WHAT WE CLAIM IS:—

1. A method of increasing the hardness of a porous film formed on the surface of a corrosion-resistant chromium-containing iron alloy by treatment of the alloy in an aqueous solution of chromic and sulphuric acids, with or without other constituents, in which the alloy bearing the porous film is subjected to electrolysis as the cathode in a hardening electrolyte from which an oxidic deposit is formed in the film pores as a result of cathodic reduction of ions derived from a soluble salt containing a metallic element in the electrolyte and/or a rise in pH within the film pores brought about by the electrolysis, the cathodic electrolysis and thereby the formation of the oxidic deposit being carried out for a period of time sufficient to harden the film but not long enough for the oxidic deposit to be formed on the film surface, and the composition of the hardening electrolyte and the current density being such that the metallic element would not be deposited on prolonging the electrolysis.

2. A method according to claim 1 in which the hardening electrolyte contains in ionic form in aqueous solution one or more of the elements aluminium, titanium, vanadium, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, copper, zinc, silicon or tin.

3. A method according to claim 2 in which the element ion in the hardening electrolyte is hexavalent chromium and in which the pH value of the hardening electrolyte is in the range of 3 to 7.5.

4. A method according to claim 2 in which the element ion is trivalent aluminium.

5. A method according to claim 2 in which the element ion is heptavalent manganese.

6. A method according to claim 2 in which the element ion is divalent nickel.

7. A method according to claim 2 in which the element ion is divalent zinc.

8. A method according to claim 1 in which the hardening electrolyte is an aqueous solution containing 0.25 to 7.5 moles per litre of CrO_3 , and sufficient base to maintain the pH value of the solution in the range 3 to 7.5.

9. A method according to claim 8 in which the aqueous solution has a pH value of 6.3 to 7.5.

10. A method according to claim 9 in which the aqueous solution contains 2.5 moles per litre of CrO_3 and 3.5 to 5.2 moles per litre of a base from the group of sodium, potassium and ammonium hydroxides or carbonates.

11. A method according to any one of claims 1 to 10 in which the alloy is stainless steel.

12. A method of increasing the hardness of a porous film on a corrosion-resistant chromium-containing iron alloy as claimed in claim 1 and substantially as hereinbefore described with reference to Examples 1 to 5.

13. An electrolyte for cathodically hardening a porous film formed on the surface of a corrosion-resistant chromium-containing iron alloy by treatment of the alloy in an aqueous solution of chromic and sulphuric acids, with or without other constituents, said electrolyte comprising 0.25 to 7.5 moles per litre of CrO_3 , and sufficient base to provide a pH value in the range 3 to 7.5.

14. An electrolyte according to claim 13, wherein the pH is in the range 6.3 to 7.5.

15. An electrolyte according to claim 14, containing 2.5 moles per litre of CrO_3 and 3.5 to 5.2 moles per litre of a base from the group of sodium, potassium and ammonium hydroxides or carbonates.

16. A corrosion-resistant chromium-containing iron alloy article having on a surface thereof a porous film increased in hardness by the method according to claim 1.

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