

PATENT SPECIFICATION

(11) 1 435 518

1 435 518

(21) Application No. 47048/72 (22) Filed 12 Oct. 1972

(23) Complete Specification filed 9 Oct. 1973

(44) Complete Specification published 12 May 1976

(51) INT CL³ C25D 9/10; C23F 17/00, 7/26

(52) Index at acceptance

C7B 15X 2F

C7U 4C 4G1 5 7C 7E 7J

(72) Inventors THOMAS ERNEST EVANS, ANTHONY CHRISTOPHER HART and WILLIAM HEALD SUTTON



(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 alloys, and is particularly applicable to stainless steel.

In our cognate Applications Nos. 25215/70 and 1245/1 (Serial No. 1,305,636) we have described a process for 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, by 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. In these Applications hardening of the film was attributed to the deposition of metallic chromium in pores in the film.

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.

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 chromium deposit is formed in the film pores, the hardening electrolyte containing in aqueous solution chromic acid and an agent, other than silico-fluoride or fluoride ions, capable of promoting the cathodic deposition of an oxidic chromium deposit within the pores of the film in prefer-

ence to metallic chromium, and the cathodic electrolysis and thereby the formation of the oxidic chromium deposit being carried out for a period of time sufficient to harden the film. The oxidic chromium deposit may consist of insoluble chromic oxide, chromic hydroxide or hydrated chromic oxide.

The initial film is formed by treatment of a corrosion-resistant chromium-containing iron alloy such as stainless steel in an aqueous solution of chromic and sulphuric acids. The treatment consists of immersing the metal to be coated in the solution with or without electrolysis which entails making the metal the anode in the solution and passing a current from a cathode in the solution. The film thus formed is porous and is made more abrasion resistant by hardening.

In highly acidic chromic acid hardening electrolytes for use according to the invention, ions produced by addition of an agent selected from CrCl_3 , HNO_3 , H_3PO_4 and CH_3COOH and ionic species derived from reaction of these agents with water and chromic acid are capable of promoting the cathodic deposition of an oxidic chromium deposit such as chromic oxide, hydrated chromic oxide and/or chromic hydroxide in preference to chromium metal. Suitable hexavalent chromium hardening electrolytes used in the process of the invention can contain approximately 0.25 to 7.5 moles per litre of CrO_3 , and can have a molar ratio of CrO_3 to ions of said agent of 20 to 1 to 500 to 1.

Typical conditions for the hardening according to the invention of blue films formed by treatment in an aqueous solution of chromic and sulphuric acids on mirror-finish Type 304 (18 to 20% chromium, 8 to 12% nickel) stainless steel are a cathodic current density of 0.05 to 4 A/dm² (amperes per square decimetre) for 2 to 30 minutes while the hardening electrolyte is at a temperature of 20 to 60°C. Local pH changes brought about electrolitically in the hardening electrolyte in proximity to the film are considered to

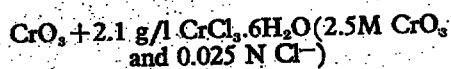
in oxidic deposition in the film pores. The colour of the oxidic chromium deposit has little or no effect on the colour of the film, although the colour of the film is usually slightly advanced in shade in the colour series brown, blue, gold, magenta, peacock and green.

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 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 colour of the film in shade. Undesirable effects are chromium 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 400 g. 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 falling, and particularly satisfactory hardening treatments may give films that withstand as many as 400 to 600 rubs.

EXAMPLE 1.

Chromic acid plus chromic chloride in an aqueous solution was employed as the hardening electrolyte. The hardening electrolyte solution used contained 250 g/l



giving a molar ratio of approximately 100:1. Test conditions were as set forth in Table 1. Tests A and B in Table 1 are outside the invention whilst Tests 1A, 1B, 1C, 1D and 1E are according to the invention.

TABLE 1

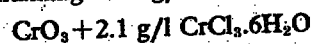
Test	Current Density A/dm ²	Time (in minutes)	Temp (°C)	Hardness (Nos. of rubs to failure)	Remarks
1A	2	15	20	360	Slight colour advancement
A	2	30	20	—	Chromium metal and/or oxide
1B	4	4	20	150	Slight colour advancement
B	4	8	20	—	Chromium metal and/or oxide deposited on top of colour film.
1C	2	30	40	600	Slight colour advancement
1D	2	30	60	400	Slight colour advancement
1E	4	10	60	400	Slight colour advancement

It is thought that all chromic acid based hardening solutions work on the same principle as that of the chromic acid plus sulphuric acid solutions. The important cathode reactions are:

- (1) Reduction of $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$.
- (2) H^+ discharge leading to pH rise and the precipitation of Cr^{III} as oxide or hydroxide.
- (3) A proportion of the Cr^{VI} is reduced to Cr^0 and deposited as chromium metal.

Whereas the presence of $\text{SO}_4^{=}$ anions seems to catalyse both the $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$ and $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^0$ it may be that other ions may preferentially or solely catalyse $\text{Cr}^{\text{VI}} \rightarrow \text{Cr}^{\text{III}}$.

It can be seen from the data set forth in Table 1 that treatment in hardening electrolytes containing 250 g/l.



was most effective at 40 to 60°C at current densities ranging from 2 to 4 A/dm² for 10 to 30 minutes, yielding good hardening without surface deposition.

The good hardness obtained did not result in unacceptable colour advancement. Provided that the process was not operated for too long a time no deposit was formed on top of the colour film. Similar results were obtained with a $\text{CrO}_3:\text{Cl}^-$ ratio of 20:1.

EXAMPLE 2.

Chromic acid plus nitric acid in aqueous solution was employed as the hardening electrolyte. The test solution contained 250

g/l CrO_3 + 2.2 g/l of 70% w/w HNO_3 solution giving a 100 : 1 molar ratio of CrO_3 : NO_3^- .

Table 2 shows the results obtained.

TABLE 2

Current Density A/dm ²	Time (In Minutes)	Temp. (°C)	Hardness (Nos. of rubs to failure)	Remarks
1	20	20	90	Oxide or hydroxide deposition within pores of the colour film as shown by slight colour advancement
2	20	20	100	" " "
4	20	20	140	" " "

- 10 As shown in Table 2 good results were obtained at 20°C with current densities ranging from 1 to 4 A/dm² for 20 minutes. The hardness obtained was comparable with that given by an aqueous solution of chromic acid plus sulphuric acid.

15 **EXAMPLE 3.**
Chromic acid plus orthophosphoric acid in aqueous solution was employed as the hardening electrolyte.

Solutions of $\text{CrO}_3/\text{H}_3\text{PO}_4$ of the following compositions were investigated, 20
 CrO_3 , 250 g/l; H_3PO_4 , 0.5 g/l i.e. 500:1 ratio
 CrO_3 , 250 g/l; H_3PO_4 , 2.5 g/l i.e. 100:1 ratio
 CrO_3 , 250 g/l; H_3PO_4 , 5.0 g/l i.e. 50:1 ratio
 CrO_3 , 250 g/l; H_3PO_4 , 12.5 g/l i.e. 20:1 ratio 25
 at current densities, temperatures and times shown in the following Table 3.

TABLE 3

$\text{CrO}_3/\text{H}_3\text{PO}_4$ Solution Ratio	Temperature (°C)	Current Density A/dm ²	Time (In Minutes)	Hardness (No. of rubs to failure)
100:1	20	0.1	20	600
50:1	40	0.2	20	600
500:1	20	1.0	20	350
20:1	60	0.2	20	500

- 30 The degree of hardening obtained was greater than that given by a chromic acid plus sulphuric acid solution. The colour advancement was acceptable and no oxide or chromium metal was deposited on top of the colour film.

35 The following trends within the ranges of variables tested in Example 3 were observed from the results of Table 3:

1. The 100 : 1 and 50 : 1 ratio solutions appeared to be slightly more effective than the 500 : 1 or 20 : 1 solutions as they gave good results at lower temperatures and/or

current densities than did the 500 : 1 or 20 : 1 solutions.

2. The lower current densities used were about equally effective. It would therefore seem that a current density of 0.1 A/dm² is preferable as the power consumption would be less. Increasing the current density to 1.0 A/dm² resulted in poorer hardening.

Use of an aqueous solution of chromic acid plus orthophosphoric acid as the hardening electrolyte is considered to have the advantages over use of a chromic acid plus sulphuric acid solution of requiring a lower current

- density and shorter electrolysis time to achieve satisfactory hardening. Furthermore greater hardening and greater resistance to finger marking of the film may be achieved. As satisfactory hardening and resistance to finger marking may be achieved at a lower current density, the tendency for metallic chromium to deposit on the film during hardening is greatly reduced.

EXAMPLE 4.

Chromic acid plus acetic acid in aqueous solution was employed as the hardening electrolyte. A solution of 250 g/l chromic acid plus 5.25 g/l acetic acid, i.e. a molar ratio of 28.5 to 1 was used at 40°C for treatment times of from 2 minutes at a current density of 14.4 A/dm² to 15 minutes at a current density of 3.6 A/dm².

Table 4 shows the results obtained.

TABLE 4.

Current Density A/dm ²	Time (in minutes)	Hardness (Nos. of rubs to failure)
3.6	15	400 +
17.2	2	100
14.4	2	160
3.6*	15	200

* solution allowed to stand for 2 days

It can be seen from the data set forth in Table 4 that a low current density of 3.6 A/dm² for a time of 15 minutes gave best hardening results.

- The resulting hardnesses were comparable to or in excess of those achieved with chromic acid plus sulphuric acid hardening solutions, for example equal to or better than 100 to 150 rubs to failure of the film. There was some evidence that a freshly-prepared solution was more effective than a solution that had been allowed to stand, possibly because on standing acetic acid may have been oxidised by the chromic acid.

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 chromium deposit is formed in the film pores, the hardening electrolyte containing in aqueous solution chromic acid and an agent, other than silico-fluoride or fluoride ions, capable of promoting the cathodic deposition of an oxidic chromium deposit within the pores of the film in preference to metallic chromium, and the cathodic electrolysis and thereby the formation of the oxidic deposit being carried out for a period of time sufficient to harden the film.

2. A method according to claim 1 in which the agent is capable of promoting the cathodic deposition of chromic oxide, hydrated chromic oxide and/or chromic hydroxide in preference to metallic chromium.

3. A method according to claim 1 or claim 2 in which the agent is one or more of chloride ion, nitrate ion, orthophosphate ion and acetate ion and ionic species derived from reactions of said ions with water and chromic acid.

4. A method according to any one of claims 1 to 3, in which the hardening electrolyte contains from 0.25 to 7.5 moles per litre of CrO₃.

5. A method according to claim 3 in which the molar ratio of CrO₃ to ions of said agent is 20:1 to 500:1.

6. A method according to claim 3 in which the agent is a chloride ion with the molar ratio of CrO₃ to chloride ions in the range of 100:1 to 20:1 and a cathode current density of 2 to 4 amperes per square decimetre.

7. A method according to claim 3 in which the agent is an orthophosphate ion, the hardening electrolyte is at a temperature of 20° C to 60° C and a cathode current density of 0.1 to 1.0 ampere per square decimetre is employed.

8. A method according to any one of claims 1 to 7 in which the alloy is stainless steel.

9. A method of increasing the hardness of a porous film on a corrosion-resistant chromium-containing iron alloy substantially as hereinbefore described with reference to Examples 1 to 4.

density and shorter electrolysis time to achieve satisfactory hardening. Furthermore greater hardening and greater resistance to finger marking of the film may be achieved.

5 As satisfactory hardening and resistance to finger marking may be achieved at a lower current density, the tendency for metallic chromium to deposit on the film during hardening is greatly reduced.

EXAMPLE 4.

Chromic acid plus acetic acid in aqueous solution was employed as the hardening electrolyte. A solution of 250 g/l chromic acid plus 5.25 g/l acetic acid, i.e. a molar ratio of 28.5 to 1 was used at 40°C for treatment times of from 2 minutes at a current density of 14.4 A/dm² to 15 minutes at a current density of 3.6 A/dm².

Table 4 shows the results obtained.

TABLE 4

Current Density A/dm ²	Time (in minutes)	Hardness (Nos. of rubs to failure)
3.6	15	400 +
17.2	2	100
14.4	2	160
3.6*	15	200

* solution allowed to stand for 2 days

It can be seen from the data set forth in Table 4 that a low current density of 3.6 A/dm² for a time of 15 minutes gave best hardening results.

25 The resulting hardnesses were comparable to or in excess of those achieved with chromic acid plus sulphuric acid hardening solutions, for example equal to or better than 100 to 150 rubs to failure of the film. There was
30 some evidence that a freshly-prepared solution was more effective than a solution that had been allowed to stand, possibly because on standing acetic acid may have been oxidised by the chromic acid.

35 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
40 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 chromium deposit is formed in the film pores, the hardening electrolyte containing in aqueous solution
45 chromic acid and an agent, other than silico-fluoride or fluoride ions, capable of promoting the cathodic deposition of an oxidic chromium deposit within the pores of the film in preference to metallic chromium, and the cathodic electrolysis and thereby the formation of the oxidic deposit being carried out for a period of time sufficient to harden the
50 film.

2. A method according to claim 1 in which the agent is capable of promoting the cathodic deposition of chromic oxide, hydrated chromic oxide and/or chromic hydroxide in preference to metallic chromium.

3. A method according to claim 1 or claim 2 in which the agent is one or more of chloride ion, nitrate ion, orthophosphate ion and acetate ion and ionic species derived from reactions of said ions with water and chromic acid.

4. A method according to any one of claims 1 to 3, in which the hardening electrolyte contains from 0.25 to 7.5 moles per litre of CrO₃.

5. A method according to claim 3 in which the molar ratio of CrO₃ to ions of said agent is 20:1 to 500:1.

6. A method according to claim 3 in which the agent is a chloride ion with the molar ratio of CrO₃ to chloride ions in the range of 100:1 to 20:1 and a cathode current density of 2 to 4 amperes per square decimetre.

7. A method according to claim 3 in which the agent is an orthophosphate ion, the hardening electrolyte is at a temperature of 20° C to 60° C and a cathode current density of 0.1 to 1.0 ampere per square decimetre is employed.

8. A method according to any one of claims 1 to 7 in which the alloy is stainless steel.

9. A method of increasing the hardness of a porous film on a corrosion-resistant chromium-containing iron alloy substantially as hereinbefore described with reference to Examples 1 to 4.



10. 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.

For the Applicants:
C. H. GREENSTREET,
Chartered Patent Agent,
Thames House, Millbank,
London, S.W.1.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY; from
which copies may be obtained.

