

PATENT SPECIFICATION

(11) 1 436 150

1 436 150

- (21) Application No. 59110/73 (22) Filed 12 Oct. 1972
- (61) Patent of Addition to No. 1 305 636 dated 14 May 1971
- (62) Divided out of No. 1 435 518
- (23) Complete Specification filed 9 Oct. 1973
- (44) Complete Specification published 19 May 1976
- (51) INT CL² C25D 9/10; C23F 17/00, 7/26
- (52) Index at acceptance
C7B 15X 2F
C7U 4C 4G1 5 7C 7B 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 the surface treatment of corrosion-resistant chromium-containing iron alloys, and is particularly applicable to stainless steel.

In our Specification No. 1,305,636 we have described and claimed a method of increasing the hardness of a film formed on the surface of a corrosion-resistant chromium-containing 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 film is subjected to electrolysis as the cathode 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 cathodic hardening treatment is preferably effected in an aqueous solution of chromic and sulphuric acid, but it may also be carried out in solutions of chromic acid containing additions of silico-fluoride or fluoride ions added either singly or in combination with sulphate ions. It is said however that these solutions are not as effective as the chromic/sulphuric acid solution since they show a much greater tendency to deposit chromium metal on to the surface of the steel.

The present invention is based on the discovery that if the cathodic hardening treatment is carried out using an aqueous solution of chromic and hydrofluoric acids, the tendency of the solution to deposit chromium on the

metal surface is reduced or even eliminated by operating at a low current density, while the hardness obtained may be even greater than that resulting from the use of a chromic/sulphuric acid solution.

According to the invention, therefore, cathodic hardening of the film is effected by subjecting the alloy bearing the film to electrolysis as the cathode in an electrolyte consisting of an aqueous solution of chromic and hydrofluoric acids, using a current density not exceeding 1 ampere per square decimetre (A/dm^2) and preferably not exceeding 0.1 A/dm^2 , 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 advantageous effects of using low current densities are shown by the results obtained in the following example. Samples of Type 304 stainless steel plate (18—20% Cr, 8—12% Ni), polished to a mirror finish, were provided with a blue coating by immersion in a solution of chromic and sulphuric acids. The coloured samples were then immersed in an aqueous hardening solution containing 250 g/l of chromic acid and 2.5 g/l of a 40% w/w solution of hydrofluoric acid, so that the molar ratio of CrO_3 to fluoride ions was 50:1. With the samples as cathodes, the solution was electrolysed for varying times at varying cathode current densities, and the hardness produced in the film was determined by a standard rubbing test which consisted in rubbing the film surface with a pencil type eraser loaded with a 400 gram weight. The conditions of electrolysis and the results of the rubbing tests are set forth in the following table, in which tests 2, 3 and 4 are in accordance with the invention, whereas test 1 is not.

TABLE

Test No.	Current Density A/dm ²	Time (in mins.)	Temp °C	Hardness (Nos. of rubs to failure)	Remarks
1	2	2	20	200	Trace of chromium deposit around edges. Slight colour advancement.
2	1	2	20	150	Slight colour advancement.
3	0.1	30	20	300	Slight colour advancement.
4	0.05	30	20	360	Slight colour advancement.

These results show clearly that satisfactory hardening without chromium deposition can be obtained at a current density of 1 A/dm² in only 2 minutes and that remarkably high hardnesses can be obtained by the use of low current densities for prolonged periods, using amounts of current not exceeding 3 A-min/dm².

Similar results were obtained with the use of hardening solutions containing chromic acid and fluoride ions in a molar ratio of 20:1.

Thus the best results were obtained according to the invention with hardening solutions containing chromic acid and fluoride ions in a molar ratio of from 20:1 to 50:1 at a current density of from 0.05 to 1 A/dm² for from 2 to 30 minutes at 20° C., the longer times being used with the lower current densities.

The hardness of films hardened by electrolysis in chromic acids/sulphuric acid solutions is generally from 100 to 150 rubs to failure using the same test.

WHAT WE CLAIM IS:—

1. A method of increasing the hardness of a 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; which comprises subjecting the alloy bearing the film to elec-

trolysis as the cathode in an electrolyte consisting of an aqueous solution of chromic and hydrofluoric acids, using a current density not exceeding 1 A/dm², 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.

2. A method according to claim 1, in which the molar ratio of chromic acid to fluoride ions is from 20:1 to 50:1.

3. A method according to claim 1 or claim 2, in which the cathode current density does not exceed 0.1 A/dm².

4. A method according to any one of claim 1 to 3, in which the amount of current passed in the cathodic electrolysis does not exceed 3 A-min/dm².

5. A method according to any one of claims 1 to 4, in which the cathodic electrolysis is carried out at a temperature of 20° C.

6. A method according to any one of claims 1 to 5, in which the alloy is stainless steel.

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

For the Applicants:

C. H. GREENSTREET,
Chartered Patent Agent,

Thames House, Millbank, London, S.W.1.

TABLE

Test No.	Current Density A/dm ²	Time (in mins.)	Temp °C	Hardness (Nos. of rubs to failure)	Remarks
1	2	2	20	200	Trace of chromium deposit around edges. Slight colour advancement.
2	1	2	20	150	Slight colour advancement.
3	0.1	30	20	300	Slight colour advancement.
4	0.05	30	20	360	Slight colour advancement.

These results show clearly that satisfactory hardening without chromium deposition can be obtained at a current density of 1 A/dm² in only 2 minutes and that remarkably high hardnesses can be obtained by the use of low current densities for prolonged periods, using amounts of current not exceeding 3 A-min/dm².

Similar results were obtained with the use of hardening solutions containing chromic acid and fluoride ions in a molar ratio of 20:1.

Thus the best results were obtained according to the invention with hardening solutions containing chromic acid and fluoride ions in a molar ratio of from 20:1 to 50:1 at a current density of from 0.05 to 1 A/dm² for from 2 to 30 minutes at 20° C., the longer times being used with the lower current densities.

The hardness of films hardened by electrolysis in chromic acids/sulphuric acid solutions is generally from 100 to 150 rubs to failure using the same test.

WHAT WE CLAIM IS:—

1. A method of increasing the hardness of a 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; which comprises subjecting the alloy bearing the film to elec-

trolysis as the cathode in an electrolyte consisting of an aqueous solution of chromic and hydrofluoric acids, using a current density not exceeding 1 A/dm², 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.

2. A method according to claim 1, in which the molar ratio of chromic acid to fluoride ions is from 20:1 to 50:1.

3. A method according to claim 1 or claim 2, in which the cathode current density does not exceed 0.1 A/dm².

4. A method according to any one of claim 1 to 3, in which the amount of current passed in the cathodic electrolysis does not exceed 3 A-min/dm².

5. A method according to any one of claims 1 to 4, in which the cathodic electrolysis is carried out at a temperature of 20° C.

6. A method according to any one of claims 1 to 5, in which the alloy is stainless steel.

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

For the Applicants:

C. H. GREENSTREET,
Chartered Patent Agent,

Thames House, Millbank, London, S.W.1.

