

PATENT SPECIFICATION

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DRAWINGS ATTACHED

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(54) TREATMENT OF A CORROSION-RESISTANT CHROMIUM-CONTAINING ALLOY

(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.

The resistance of stainless steel, whether austenitic, ferritic or martensitic, to corrosion and abrasion is well known but nevertheless susceptible of improvement. Our main object in the invention is to improve the resistance of coloured stainless steel and other chromium-containing alloys to both corrosion and abrasion; we aim also at improving the resistance of uncoloured stainless steels and other chromium-containing alloys at least to corrosion.

The production of coloured films on stainless steel by treatment with solutions containing chromic and sulphuric acid has been known for many years as a method of colouring stainless steel, being first described in British Specification No. 275,781. Normally the processes involve simple immersion of the steel in the treating solution, and among these immersion processes are those described in our British Specifications Nos. 1,122,172 and 1,122,173, in each of which the solution of chromic acid also contains sulphuric acid and in the second of which it contains manganous sulphate as well. By means of these processes very attractive colours can be produced on stainless steel.

In the production of coloured films the steel must be left in the solution for a specific period of time before any recognisable colour appears on the surface. We have found, however, that some film is formed on the surface of the steel before any colour is detectable, the steel retaining its natural appearance. It

is likely that the colour is caused by interference effects produced only when a certain thickness of film is reached, these effects, and therefore the colours, varying with the thickness of the film.

According to the invention 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, is increased by subjecting the alloy bearing the film to electrolysis as the cathode in an electrolyte from which chromium can be deposited. 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. The mechanism by which the film is hardened is uncertain, although possibly metallic chromium is deposited.

Whatever the mechanism, the hardening of the film is shown by tests to increase the resistance to corrosion, whether there has been a change in colour or not. It is difficult to demonstrate improved resistance to abrasion by tests on steel or other alloy which has not changed its colour, but easy to do this when the colour has changed, and there is no reason to suppose that improved resistance to abrasion is not obtained when the film has been hardened but the colour has not changed.

A test for resistance to corrosion involves comparison of two panels which have been identically treated in a solution of chromic and sulphuric acids, but one only of which has also been cathodically treated to harden the film, and both of which are tested by being sprayed with an aqueous solution containing 50 g/l sodium chloride and 0.26 g/l cupric chloride to which acetic acid has been added to adjust the pH to 3.2: the solution is sprayed at a temperature of 49°C and a rate of 1.5 ml. per hour per 80 cm² in a closed cabinet.

The degree of staining of the panels as a

result of the spraying is observed visually and assessed as shown by the accompanying drawing. This shows seven panels classified as follows:—

- 5 1. Unstained.
2. Lightly stained.
3. Light-to-moderate staining.
4. Moderate staining.
5. Moderate-to-heavy staining
- 10 6. Heavy staining.
7. Very heavy staining.

15 If the film has been hardened, the degree of staining will be at least one class lower than that on the comparative panel which has not been cathodically treated.

A test for resistance to abrasion involves rubbing similar panels with a pencil eraser containing abrasive particles and carried by a pivoted arm under a given load, the eraser

being moved forwards and backwards over the same area of the panel, which is thus subjected to a number of rubs. The eraser and the load are so chosen that an untreated coloured film is removed by 4 rubs at the most. If the cathodically treated film resists at least 40 rubs before it is removed, it is hardened.

The colouring treatment can be successfully operated over wide limits of solution concentration and temperature, but in order to achieve reproducibility of results and good colour matching it is necessary to ensure that these variables and also the time of immersion are closely controlled. It is found that desired colours are most easily obtained on austenitic and ferritic steel when the composition of the solution and the temperature are as follows:—

	Range	Preferred
CrO ₃ concentration	200—400 g/l	240—300 g/l
H ₂ SO ₄ concentration	350—700 g/l	450—550 g/l
Temperature	65—80°C	68—72°C

40 It is preferred not to exceed the preferred concentrations in order to avoid the risk of supersaturation of the solution with consequential formation of a precipitate which may not dissolve, with the further consequence that the composition of the solution may change.

45 Under the optimum conditions colouring of austenitic and ferritic steel takes between about 7 and 15 minutes, depending on the shade desired. At lower temperatures the time required for colouring is lengthened, whilst at higher temperatures the time is shorter and consequently colour control may be difficult. Under the optimum conditions a useful uncoloured film is formed in about 5 minutes, a blue film is about 8 minutes and a gold film in about 10 minutes. It is surprisingly found that if the steel is in the marten-

60 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. These solutions are not, however, as effective as the chromic/sulphuric 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 metal can normally be plated, for example, a trivalent chromium salt dissolved in di-methyl formamide solution.

75 The concentrations of CrO₃ and sulphuric acid in the preferred solution (the electrolyte) may vary widely, but for the best results the concentration of CrO₃ should be at least 25 g/l and preferably at least 250 g/l, and may be as high as 850 g/l or more, and the concentration of sulphuric acid may be as low as 0.1 g/l or as high as 10 g/l or more. The temperature may vary from 20 to 80°C and the current density may be as low as 0.6 or as high as 30 amp/dm². Preferably the electrolyte contains from 240 to 260 g/l CrO₃ and from 1.0 to 2.6 g/l H₂SO₄, the temperature is from 25 to 40°C and the current density is from 2.4 to 9.6 amp/dm². In accordance with the variations in these factors, the duration of the treatment may then be as short as 2 minutes or as long as 30 minutes. This cathodic treatment usually produces a marginal change in colour.

95 Care must be exercised during the treatment since chromium metal 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.

5 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 colouring treatment in order to avoid the possibility of staining or marking of the unhardened film. Delay in applica-
10 tion of the hardening treatment does not, however, prevent it being carried out effectively.

Both the colouring 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 colouring solution gently so as to maintain uniformity of temperature throughout it, but not to agitate either solution.

20 It will be seen that, for the best colour control, a solution containing more sulphuric acid than chromic acid should be used, but that in the cathodic treatment it is desirable to make the proportion of chromic acid to sulphuric acid high. Nevertheless, for
25 example, the same solution can be used in both steps, the colouring being effected without the passage of current and the cathodic treatment by the subsequent passage of
30 current, though the development of the colour is very slow. One such solution contains 300

g/l CrO_3 and 100 g/l H_2SO_4 and is maintained at 70°C in both steps.

Some examples will now be given.

Example 1

35 Panels of 18/8 chromium-nickel austenitic stainless steel were immersed in a solution containing 300 g/l CrO_3 and 550 g/l H_2SO_4 at a temperature of 70°C . One set of the panels was immersed for about 5 minutes to
40 form uncoloured films leaving the natural colour of the steel, a second set for about 8 minutes to form blue films and a third set for about 10 minutes to form gold films. Some of the panels in each set were put aside
45 after the treatment for subjection to the corrosion test, and the remainder of each set were subjected to the cathodic hardening treatment in an electrolyte containing 250 g/l CrO_3 and 2.5 g/l sulphuric acid at a temperature of
50 40°C for a period of time adequate to harden the film but not so long that any chromium became visible on the film surface as a white deposit. In another series of tests, similar
55 panels were treated in the same way except that only films of natural and blue colour were produced. The results of the corrosion tests on all these panels are shown in Table 1, the degree of staining being indicated numerically
60 by reference to the drawing.

TABLE 1

Test	Treatment	Colour	Degree of staining
1	Uncoloured	Natural	4
	Coloured	Blue	6
	Coloured	Gold	6
	Uncoloured and hardened	Natural	2
	Coloured and hardened	Blue	2
	Coloured and hardened	Gold	2
2	Uncoloured	Natural	3
	Coloured	Blue	5
	Uncoloured and hardened	Natural	1
	Coloured and hardened	Blue	1

It will be seen that the resistance to staining of the panels subjected to the hardening treat-

ment was always at least two classes better than that of those bearing unhardened films. 65

Example 2

Panels of 17% chromium ferritic steel were treated as in Example 1 to produce uncoloured and blue films, some were left unhardened and

some were hardened as in Example 1, and all were similarly tested with the results shown in Table 2.

5

TABLE 2

Treatment	Colour	Degree of staining
Uncoloured	Natural	4
Coloured	Blue	5
Uncoloured and hardened	Natural	3
Coloured and hardened	Blue	3

Example 3

10 Panels of an 18/8 chromium-nickel stainless steel were coloured blue by immersion in an aqueous solution containing 300 g/l CrO_3 and 550 g/l sulphuric acid at 70°C. for 8 minutes. The blue films thus formed were removed from some of these after from 2 to 4 rubs under a load of 500 g in the test described above. The other panels were then given cathodic treatment in aqueous solutions

containing various amounts of chromic acid under various conditions of temperature, time of exposure (i.e. adequate to harden the film but not so long that chromium became visible as a white deposit on the film) and current density and then rubbed. The tests were stopped after 200 rubs. The results are shown in Table 3 below in which "200+" means that the coating has not failed at that stage.

20

25

TABLE 3

Solution composition	Cathodic Treatment			Rubs to failure
	Temperature °C	Time minutes	Current density amps/dm ²	
250g/l CrO ₃ +2.5g/l H ₂ SO 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
250g/l CrO ₃ +2.5g/l H ₂ SO 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
25g/l CrO ₃ +2.5g/l H ₂ SO ₄	40	20	2.4	120
" "	40	7	4.8	140
" "	40	10	4.8	60
100g/l CrO ₃ +2.5g/l H ₂ SO ₄	40	10	2.4	40
" "	40	20	2.4	105
" "	40	7	4.8	120
" "	40	10	4.8	70
400g/l CrO ₃ +2.5g/l H ₂ SO ₄	40	10	2.4	160
" "	40	20	2.4	180
" "	40	7	4.8	180
" "	40	10	4.8	200+
500g/l CrO ₃ +2.5g/l H ₂ SO ₄	40	10	2.4	80
" "	40	20	2.4	90
" "	40	7	4.8	180
" "	40	10	4.8	120
750g/l CrO ₃ +2.5g/l H ₂ SO ₄	40	10	2.4	180
" "	40	20	2.4	140
" "	40	7	4.8	120
" "	40	10	4.8	80
250g/l CrO ₃ +10g/l H ₂ SO ₄	40	20	2.4	60
" "	40	10	4.8	70
250g/l CrO ₃ +100g/l H ₂ SO ₄	40	20	2.4	60
" "	40	10	4.8	60

Example 4

Panels of three ferritic stainless steels were treated, namely 17% chromium, 13% chromium and 17% chromium, 1% molybdenum, steels respectively. The panels were all treated in an aqueous solution of chromic and sulphuric acids to develop a blue colour, 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 (i.e. long enough to harden the film but not deposit chromium as a white deposit on the film) at a current density of 2.4 A/dm², and these maintained the colour for from 80 to 160 rubs.

Alloys other than steel on which films can be formed and then satisfactorily cathodically hardened include iron-based nickel-chromium-molybdenum alloys such as an alloy containing 37% nickel, 18% chromium, 5% molybdenum, 1.2% titanium and 1.2% aluminium; cobalt-based alloys such as that containing 21% chromium, 21% nickel and 13% molybdenum; and nickel-chromium alloys, such as an alloy containing 30% chromium and 1% titanium, the remainder being nickel.

It is possible to produce different colours on different areas of the alloy 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 colouring treatment, and then subjecting the whole alloy to the cathodic hardening treatment.

It is an advantage of the invention that alloys bearing hardened coloured films can be considerably deformed without changing the colour. Thus coloured chromium-containing steel sheets can be deep-drawn or passed through patterned rolls to increase their rigidity, and will still retain their colour. Another advantage is that hardened coloured films resist boiling water well, so it is possible to produce kitchen utensils such as saucepans of stainless steel in attractive colours which are not rapidly lost in use.

WHAT WE CLAIM IS:—

1. 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.

2. A method of treating stainless steel in which a film is first produced on the surface of the steel by immersion in an aqueous solution of chromic and sulphuric acids, with or without other constituents, and the steel bearing the film is then subjected to electrolysis as the cathode in an aqueous solution of chromic acid and sulphuric acid 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.

3. A method according to claim 2 in which the initial immersion in the solution of chromic and sulphuric acids is carried on for long enough to produce a coloured film.

4. A method according to claim 3 in which the production of the coloured film is effected by immersing the steel in a solution containing from 200 to 400 g/l CrO_3 and from 350 to 700 g/l H_2SO_4 at a temperature between 65 and 80°C.

5. A method according to claim 4 in which the solution contains from 240 to 300 g/l CrO_3 and from 450 to 550 g/l H_2SO_4 and its temperature during the immersion is from 68 to 72°C.

6. A method according to any of claims 2 to 5 in which the electrolyte in which the cathodic treatment is effected is a solution containing from 25 to 850 g/l CrO_3 and from 0.1 to 10 g/l H_2SO_4 , and during the electrolysis the temperature of the solution is from 20 to 80°C and the current density is from 0.6 to 30 amp/dm².

7. A method according to claim 6 in which the electrolyte contains from 240 to 260 g/l CrO_3 and from 1.0 to 2.6 g/l H_2SO_4 , the temperature is from 25 to 40°C and the current density is from 2.4 to 9.6 amp/dm².

8. A method according to any preceding claim in which different colours are produced on different parts of the alloy 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 film-forming treatment, and then subjecting the whole alloy to the cathodic hardening treatment.

9. Stainless steel treated by a method according to any of claims 2 to 7.

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Example 4

Panels of three ferritic stainless steels were treated, namely 17% chromium, 13% chromium and 17% chromium, 1% molybdenum, steels respectively. The panels were all treated in an aqueous solution of chromic and sulphuric acids to develop a blue colour, 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 (i.e. long enough to harden the film but not deposit chromium as a white deposit on the film) at a current density of 2.4 A/dm^2 , and these maintained the colour for from 80 to 160 rubs.

Alloys other than steel on which films can be formed and then satisfactorily cathodically hardened include iron-based nickel-chromium-molybdenum alloys such as an alloy containing 37% nickel, 18% chromium, 5% molybdenum, 1.2% titanium and 1.2% aluminium; cobalt-based alloys such as that containing 21% chromium, 21% nickel and 13% molybdenum; and nickel-chromium alloys, such as an alloy containing 30% chromium and 1% titanium, the remainder being nickel.

It is possible to produce different colours on different areas of the alloy 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 colouring treatment, and then subjecting the whole alloy to the cathodic hardening treatment.

It is an advantage of the invention that alloys bearing hardened coloured films can be considerably deformed without changing the colour. Thus coloured chromium-containing steel sheets can be deep-drawn or passed through patterned rolls to increase their rigidity, and will still retain their colour. Another advantage is that hardened coloured films resist boiling water well, so it is possible to produce kitchen utensils such as saucepans of stainless steel in attractive colours which are not rapidly lost in use.

WHAT WE CLAIM IS:—

1. 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.

2. A method of treating stainless steel in which a film is first produced on the surface of the steel by immersion in an aqueous solution of chromic and sulphuric acids, with or without other constituents, and the steel bearing the film is then subjected to electrolysis as the cathode in an aqueous solution of chromic acid and sulphuric acid 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.

3. A method according to claim 2 in which the initial immersion in the solution of chromic and sulphuric acids is carried on for long enough to produce a coloured film.

4. A method according to claim 3 in which the production of the coloured film is effected by immersing the steel in a solution containing from 200 to 400 g/l CrO_3 and from 350 to 700 g/l H_2SO_4 at a temperature between 65 and 80°C .

5. A method according to claim 4 in which the solution contains from 240 to 300 g/l CrO_3 and from 450 to 550 g/l H_2SO_4 and its temperature during the immersion is from 68 to 72°C .

6. A method according to any of claims 2 to 5 in which the electrolyte in which the cathodic treatment is effected is a solution containing from 25 to 850 g/l CrO_3 and from 0.1 to 10 g/l H_2SO_4 , and during the electrolysis the temperature of the solution is from 20 to 80°C and the current density is from 0.6 to 30 amp/dm^2 .

7. A method according to claim 6 in which the electrolyte contains from 240 to 260 g/l CrO_3 and from 1.0 to 2.6 g/l H_2SO_4 , the temperature is from 25 to 40°C and the current density is from 2.4 to 9.6 amp/dm^2 .

8. A method according to any preceding claim in which different colours are produced on different parts of the alloy 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 film-forming treatment, and then subjecting the whole alloy to the cathodic hardening treatment.

9. Stainless steel treated by a method according to any of claims 2 to 7.

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