

471711 14

PATENT SPECIFICATION

NO DRAWINGS

Inventors: HOWARD JAMES, COLIN GEORGE SMITH and LESLIE GOODRIDGE
TOTTLE

L122,172



L122,172

Date of filing Complete Specification: 9 March, 1967.

Application Date: 9 March, 1966.

No. 10344/66.

Complete Specification Published: 31 July, 1968.

© Crown Copyright 1968.

Index at acceptance: —C7 U(3, 4C, 4G1, 4K, 5, 7C); C7 B2F

Int. Cl.: —C 23 f 7/26

COMPLETE SPECIFICATION

Colouring Stainless Steel

5 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:—

10 Because of their attractive, bright and lustrous appearance nickel-containing stainless steels are used increasingly in architecture, as motor car trim, and in domestic articles and similar equipment. While the natural colour of these metals is pleasing, there is at the same time a demand for a different appearance on them, and in particular for a coloured finish in which the bright, lustrous appearance of the metal is retained. Our object in this invention is to satisfy this demand.

20 Many different processes for producing coloured coatings on stainless steel are known. These processes include anodic oxidation in aqueous solutions of suitable salts, a direct current being used.

25 In the course of our work, we have found that nickel-containing stainless steels may be coloured gold by immersing the steel in an aqueous solution of chromic acid containing between 50 and 1000 grams of CrO_3 per litre, that is 0.5 to 10 molar, for a period of time which depends on the concentration of the solution, the temperature and the shade of the gold colour to be imparted to the steel. As the temperature is raised, so is the period of immersion necessary for colouring reduced. The gold colour can be obtained at room temperature although the period of immersion required is then long, and we have found it best to work at a temperature of at least 65°C . so as to obtain results in a reasonably short time.

We find that the shade of the gold colour produced deepens with the time of immersion and that eventually it reaches what may be called a "terminal" colour for any given temperature of the solution, that is, it is impossible to produce a deeper gold colour than the terminal colour without corrosion of the steel taking place and the coloured coating becoming non-adherent. For example, in a solution of chromic acid having a concentration of 250 grams per litre calculated as CrO_3 , at a temperature of 65°C , 18% chromium 8% nickel stainless steel is lightly coloured after 2½ hours, gold-brown after 3 hours, and has a terminal dark gold-brown colour after 4 hours. If the temperature is raised to 80°C , a gold colour appears in less than 2 hours, and a terminal light gold-brown colour in less than 3 hours. If the temperature is further raised to 95°C , a terminal gold colour appears in about 35 minutes. The deeper the desired shade of gold to be produced, the cooler must be the solution, and therefore the longer the period of immersion. Good reproducibility of the colour shade can be achieved provided that the temperature and concentration of the solution are accurately controlled, and the period of immersion not allowed to vary by more than a few minutes.

We have now found that the most useful dark gold terminal colour is obtained on the steel to be coloured if the concentration of chromic acid is in a narrow range and the solution is further acidified by the addition of sulphuric acid. According to the invention, we colour nickel-containing stainless steel by immersing the steel in an aqueous solution containing from 520 to 580 g/l of chromic acid calculated as CrO_3 and sufficient sulphuric acid to make the ratio of the weights of chromic acid to sulphate ion pre-

[Price 4s. 6d.]

sent as sulphuric acid between 3:1 and 7:1, at a temperature of 65° to 75°C. The period of time of immersion depends on the colour to be imparted to the steel. The preferred conditions are a temperature of 70°C and concentrations of 550 g/l chromic acid calculated as CrO₃ and 60 ml per litre of sulphuric acid of S.G. 1.84 giving a weight ratio of chromic acid to sulphate ion of about 5:1. At this temperature the steel colours quickly, and, incidentally, may be handled by operators wearing ordinary gloves; the ratio of chromic acid to sulphate gives a good depth of shade. We find that under these conditions we can obtain in about 15 minutes a terminal gold colour which is darker than that obtained hitherto, and we further find that the film is superior in its resistance to atmospheric corrosion to those obtained using different temperatures or concentrations.

We find that trivalent chromium ions tend to build up slowly in the solution, and in time impair the ability of the solution to colour steel. At concentrations of Cr⁺⁺⁺ ion above about 13 grams per litre the effect becomes serious enough virtually to prevent any colouring. Accordingly the concentration of trivalent chromium ions should be kept low, preferably below 10 g/l, and we find that this can be done by electrolysis the solution continuously between a large anode and a small cathode so that in effect it becomes the electrolyte in an electrolytic cell and trivalent chromium ions are oxidised to the hexavalent state. This may preferably be done by withdrawing solution into a subsidiary tank, electrolysis it and returning it to the main bath.

It is possible to obtain blue to red colours on stainless steel by first forming a gold-brown colouring and then heating the coloured steel in air at from 300 to 700°C, preferably around 550°C, until it reaches the desired colour. For instance, an article having a gold coating may be held in a gas flame until the desired colour appears, normally in under 5 minutes, or may be passed through a furnace on a conveyor belt, through a controlled temperature zone.

If a colour other than gold is to be produced by heating, then we prefer that the gold colour initially produced should be a dark terminal colour. In this way we find that we get more reproducible results.

The coloured coatings produced have a lustrous metallic appearance and exhibit the same resistance to scratching and abrasion as the original surface of the metal on which the coating is formed. The coatings further do not dissolve in water, do not take dyes and are resistant to atmospheric attack. They are however attacked by hydrochloric acid. Use can be made of this fact to provide designs or lettering in one or more colours

on an article. For example "stop-off" materials may be applied which will protect the surface of the steel against colour changes from the chromic acid and heat treatments, or prevent removal of the colour by a reducing acid, e.g. dilute hydrochloric. The resist may be applied by any of the conventional methods for printing or applying patterns such as stencilling, photographic techniques, freehand drawing, and silk-screen printing, and must be stable under the particular conditions for the duration of the colouring or removal treatment but must be readily removable after use by some means which does not harm the colour surfaces. Using combinations of the methods described of colouring, removal, and recolouring, patterns, designs, pictures, or letters of many colours and combinations of colours may be reproduced on the surface of the steel.

The process can be repeated to provide printing or reproduction of different colours, provided that colours already applied are suitably protected.

The process according to the invention may be used to print information on the surface of stainless steel by photographic techniques using a photoresist. The surface of the steel is covered with a photoresist which is acid-resistant after development, exposed to light transmitted through a photographic negative or positive and developed, the surface of the steel is coloured by immersion in the aqueous solution, and the remainder of the photoresist layer is subsequently removed from the surface. While satisfactory results are obtained using the wide range of concentrations of chromic acid which we have mentioned earlier, that is 50 to 1000 g/l calculated as CrO₃, best results are once again obtained in the range of 520 to 580 g/l. The colouring of the steel may be enhanced, according to our copending application No. 26970/66 (Serial No. 1122173) by the addition to the aqueous solution of from 0.3 to 50 g/l of manganous sulphate.

It is desirable that the metal to be coloured should have a smooth uniform surface, for example such as may be obtained by electropolishing, abrasion by emery paper or buffing with a cloth pad. The colouring process according to the invention is particularly applicable to nickel-containing stainless steel sheets such as are intended for architectural purposes, and the standard smooth finish of such sheets is satisfactory. In all cases, however, the metal should be cleaned before immersion in the colouring solution, for examples by washing with warm detergent solution and rinsing with water, or by washing with suitable solvent. Alternatively the metal may be subjected to cathodic cleaning in the manner commonly used in the metal finishing industry.

The invention is concerned with hot con-

70

75

80

85

90

95

100

105

110

115

120

125

130

centrated solutions of chromic acid, and it is well known that such solutions will tend to etch steel tanks in which they are kept. For this reason we prefer to use a tank of plastics material, specifically one made of polypropylene. Such a tank may still be attacked by hot chromic acid if the plastics material is in a state of stress, and we have found that a very satisfactory way of minimising the risk of the plastics material being under stress is to support the polypropylene tank in a water bath. This serves to reduce mounting stresses in the polypropylene tank, and provides ready temperature control of the contents of the tank.

Some examples will now be given:—

EXAMPLE 1.

In a solution of chromium trioxide containing 550 g/l chromic acid calculated as CrO_3 and 60 ml per litre of sulphuric acid of S.G. 1.84 used at a temperature of 70°C , 18/8 stainless steel reached a terminal colour of deep gold after 15 minutes. The deep gold-coloured film was raised to a temperature of 500°C and changed to red in 3 minutes, to purple in 4 minutes and to blue in 5 minutes. All of these films were resistant to industrial atmospheric attack and corrosion by dilute sulphuric acid.

EXAMPLE 2.

A sheet of 18/8 stainless steel was cleaned and covered with the photo-sensitive emulsion sold under the Trade Mark Kodak KMER Photo-resist. The surface was then exposed to light through a negative in a simple photographic enlarging apparatus and developed. The steel was then placed in a solution of the same composition as that used in Example 1 but with the addition of 4 g/l of manganous sulphate, at a temperature of 70°C , and was kept immersed in the solution for seven minutes after which time a gold colour had appeared on the surface. The steel was then removed from the solution and the photo-resist washed off to leave a positive image of the original negative. The experiment was repeated, except that the steel was left in the solution for nine minutes. The positive image was then coloured darker gold.

EXAMPLE 3.

A sheet of stainless steel was covered by a photo-resist and exposed to light as described in Example 2. The steel was then immersed in a solution containing 550 g/l of chromic acid calculated as CrO_3 and sulphuric acid such as to make the ratio of the weights of the chromium trioxide to the sulphate ion present as sulphuric acid 5:1. An addition of 2 g/l of manganous sulphate was made to the solution and the solution brought to a temperature of 70°C . A terminal gold

colour was produced in seven minutes, and after the photoresist had been removed, a positive picture was delineated in gold on the surface of the steel.

WHAT WE CLAIM IS:—

1. A process in which nickel-containing stainless steel is coloured by immersing the steel in an aqueous solution containing from 520 to 580 g/l of chromic acid calculated as CrO_3 and sufficient sulphuric acid to make the ratio of the weights of chromic acid to sulphate ion present as sulphuric acid between 3:1 and 7:1 at a temperature of 65° to 75°C .

2. A process according to claim 1 in which the aqueous solutions contains 550 g/l of chromic acid calculated as CrO_3 and 60 ml per litre of sulphuric acid of S.G. 1.84 and is at a temperature of 70°C .

3. A process according to claim 1 or claim 2 in which the concentration of trivalent chromium ions in the solution is kept below 10 g/l by electrolysis of the solution continuously between a large anode and a small cathode.

4. A process according to claim 3 in which solution is withdrawn into a subsidiary tank, electrolysed and returned to the main bath.

5. A process according to any one of claims 1 to 4 in which the coloured steel is subsequently heated in air at from 300 to 700°C .

6. A process according to any one of claims 1 to 5 for the printing of information on the surface of nickel-containing stainless steel, in which the surface is covered with a photoresist which is acid-resistant after development, exposed to light transmitted through a photographic negative or positive and developed, the surface of the steel is coloured by immersion in the aqueous solution, and the remainder of the photoresist layer is subsequently removed from the surface.

7. A process according to any one of the preceding claims in which the aqueous solution is contained in a polypropylene tank supported in a water bath.

8. A process according to claim 1 substantially as described with reference to Example 1 herein.

9. A process according to claim 4 substantially as described with reference to Example 2 or Example 3 herein.

10. Stainless steel coloured by a process according to any one of claims 1 to 9.

11. Stainless steel having information printed on it by a process according to any one of claims 5 to 7.

For the Applicants:—

GILL, JENNINGS & EVERY,

Chartered Patent Agents,

51/52, Chancery Lane, London, W.C.2.



* C L M S *

16

1,122,172

3

centrated solutions of chromic acid, and it is well-known that such solutions will tend to etch steel tanks in which they are kept. For this reason we prefer to use a tank of plastics material, specifically one made of polypropylene. Such a tank may still be attacked by hot chromic acid if the plastics material is in a state of stress, and we have found that a very satisfactory way of minimising the risk of the plastics material being under stress is to support the polypropylene tank in a water bath. This serves to reduce mounting stresses in the polypropylene tank, and provides ready temperature control of the contents of the tank.

Some examples will now be given:—

EXAMPLE 1.

In a solution of chromium trioxide containing 550 g/l chromic acid calculated as CrO_3 , and 60 ml per litre of sulphuric acid of S.G. 1.84 used at a temperature of 70°C , 18/8 stainless steel reached a terminal colour of deep gold after 15 minutes. The deep gold-coloured film was raised to a temperature of 500°C and changed to red in 3 minutes, to purple in 4 minutes and to blue in 5 minutes. All of these films were resistant to industrial atmospheric attack and corrosion by dilute sulphuric acid.

EXAMPLE 2.

A sheet of 18/8 stainless steel was cleaned and covered with the photo-sensitive emulsion sold under the Trade Mark Kodak KMER Photo-resist. The surface was then exposed to light through a negative in a simple photographic enlarging apparatus and developed. The steel was then placed in a solution of the same composition as that used in Example 1 but with the addition of 4 g/l of manganous sulphate, at a temperature of 70°C , and was kept immersed in the solution for seven minutes after which time a gold colour had appeared on the surface. The steel was then removed from the solution and the photo-resist washed off to leave a positive image of the original negative. The experiment was repeated, except that the steel was left in the solution for nine minutes. The positive image was then coloured darker gold.

EXAMPLE 3.

A sheet of stainless steel was covered by a photo-resist and exposed to light as described in Example 2. The steel was then immersed in a solution containing 550 g/l of chromic acid calculated as CrO_3 , and sulphuric acid such as to make the ratio of the weights of the chromium trioxide to the sulphate ion present as sulphuric acid 5:1. An addition of 2 g/l of manganous sulphate was made to the solution and the solution brought to a temperature of 70°C . A terminal gold

colour was produced in seven minutes, and after the photoresist had been removed, a positive picture was delineated in gold on the surface of the steel.

WHAT WE CLAIM IS:—

1. A process in which nickel-containing stainless steel is coloured by immersing the steel in an aqueous solution containing from 520 to 580 g/l of chromic acid calculated as CrO_3 , and sufficient sulphuric acid to make the ratio of the weights of chromic acid to sulphate ion present as sulphuric acid between 3:1 and 7:1 at a temperature of 65° to 75°C .

2. A process according to claim 1 in which the aqueous solutions contains 550 g/l of chromic acid calculated as CrO_3 , and 60 ml per litre of sulphuric acid of S.G. 1.84 and is at a temperature of 70°C .

3. A process according to claim 1 or claim 2 in which the concentration of trivalent chromium ions in the solution is kept below 10 g/l by electrolysis the solution continuously between a large anode and a small cathode.

4. A process according to claim 3 in which solution is withdrawn into a subsidiary tank, electrolysed and returned to the main bath.

5. A process according to any one of claims 1 to 4 in which the coloured steel is subsequently heated in air at from 300 to 700°C .

6. A process according to any one of claims 1 to 5 for the printing of information on the surface of nickel-containing stainless steel, in which the surface is covered with a photo-resist which is acid-resistant after development, exposed to light transmitted through a photographic negative or positive and developed, the surface of the steel is coloured by immersion in the aqueous solution, and the remainder of the photoresist layer is subsequently removed from the surface.

7. A process according to any one of the preceding claims in which the aqueous solution is contained in a polypropylene tank supported in a water bath.

8. A process according to claim 1 substantially as described with reference to Example 1 herein.

9. A process according to claim 4 substantially as described with reference to Example 2 or Example 3 herein.

10. Stainless steel coloured by a process according to any one of claims 1 to 9.

11. Stainless steel having information printed on it by a process according to any one of claims 5 to 7.

For the Applicants:—

GILL, JENNINGS & EVERY,
Chartered Patent Agents,

51/52, Chancery Lane, London, W.C.2.