

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Colouring Stainless Steel

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:—

It is known that the surfaces of stainless steels can be coloured by immersion in solutions containing chromium trioxide and sulphuric acid. The colour changes as the steel remains immersed in the solution. We find that there is what may be called, a "terminal" colour for any given concentration of the solution, that is, it is impossible to go further along the scale of colours than the terminal colour without corrosion of the steel taking place and the coloured coating becoming non-adherent. In some solutions, the order to which the colours are formed is slate - blue - yellow - red - green, whereas in other solutions only a gold colour can be formed. Good reproducibility of colouring 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.

In the course of our work, we have found that nickel-containing stainless steels may be coloured by immersing the steel in solutions which may vary widely in concentration, for example from 50 to 1000 grams of chromium trioxide (CrO_3) per litre of water, together with sulphuric acid which may be present in so small an amount that the ratio of the weights of chromium trioxide to sulphate ion added as sulphuric acid is only 100:1, or in much greater amounts, so that the ratio is up to, say, 1:1, for a period of time which

depends on the concentration of the solution, the temperature and the shade of the colour to be imparted to the steel. As the temperature is raised, so is the period of immersion necessary for colouring reduced. The best terminal gold colour is obtained, as explained in our Application No. 10344/66, when the concentration of chromium trioxide is in the narrow range of from 520 to 580 g/l of water and the solution is further acidified by the addition of sulphuric acid to make the ratio of the weights of the chromium trioxide to the sulphate ion added as sulphuric acid from 3:1 to 7/1.

We have now surprisingly found that the formation of a coloured film on stainless steel from any chromium trioxide-sulphuric acid solution is speeded by the addition to the solution of manganous sulphate ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) in the range of 0.3 g/l to 50 g/l. Below 0.3 g/l the addition has no appreciable effect on the speed of production of the coloured film, and above 50 g/l the production of the coloured film is not readily controllable. We prefer to make the addition of manganous sulphate to the solution in the range of 4 to 5 g/l.

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 of the solution continuously between a large anode and a small cathode so that in effect it becomes the electrolyte in an electrolytic

[Price 4s. 6d.]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

cell and trivalent chromium ions are oxidised to the hexavalent state. This may preferably be done by withdrawing solution into a subsidiary tank, electrolysing it and returning it to the main bath.

Once stainless steel has been coloured gold in a suitable solution according to the invention, it is possible to alter the colour by heat treatment, this heat treatment advancing the colour of the steel along the scale of colours. For example, it is possible to obtain blue or red colours on stainless steel by first forming a gold or 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.

Some Examples will now be given:—

EXAMPLE 1

A solution was prepared containing 300 g/l of chromium trioxide and 600 g/l of sulphuric acid, and was brought to a temperature of 70°C. Pieces of 18/8 chromium-nickel stainless steel were immersed for the following times and coloured accordingly:—

15 minutes	blue
20 minutes	red
25 minutes	greenish-red

An addition of 0.6 g/l of manganous sulphate to an identical solution was then made and pieces of the same stainless steel were immersed in this to give the following results:—

12 minutes	blue
16 minutes	red
18 minutes	greenish-red

When 4 g/l of manganous sulphate was added to an identical solution, pieces of the same stainless steel were coloured in the times shown below:—

7 minutes	blue
9 minutes	red
11 minutes	greenish-red

With addition of 25 g/l and 50 g/l, the blue colour alone appeared in 3 and 2 minutes respectively. After about 4 minutes the film became powdery and lost its ability to adhere to the surface of the steel.

EXAMPLE 2

A solution was prepared as described in our Application No. 10344/66 (Serial No. 1,122,172). It contained 550 g/l of chrom-

ium trioxide and was acidified by the addition of sulphuric acid to make the ratio of the weights of the chromium trioxide to the sulphate ion added as sulphuric acid 5:1. Some of this solution was then brought to a temperature of 70°C. A piece of 18/8 stainless steel was immersed in the solution and a terminal gold colour was produced in 13 minutes.

1 g/l of manganous sulphate was added to a further part of the solution and another piece of the stainless steel was then immersed and the terminal gold colour was produced in 8 minutes. When the steel was left in the bath for 9 minutes, surprisingly a blue sheen was obtained on the surface of the steel and, in contra-distinction to the terminal gold colour, could not be heat-treated to change its colour.

The same solution with an addition of 2 g/l of manganous sulphate produced a terminal gold colour on the steel in 7 minutes and the blue sheen appeared in 9 minutes.

With an addition of 25 g/l of manganous sulphate the terminal gold colour was obtained in 3 minutes and the blue sheen in 7 minutes.

With an addition of 50 g/l of manganous sulphate to the solution, the blue sheen appeared in 5 minutes. After 6 minutes, however, the film powdered and lost its ability to adhere to the metal surface.

In solutions containing 150 to 300 g/l of chromium trioxide, the terminal colour green is only reached after the colours have run through the colour sequence blue - yellow - red - green. None of these colours may be changed by subsequent heat-treatment. It is possible, on the other hand, to revert to a colour one earlier in the scale by treatment with a suitable reducing agent. This allows scope for colour-adjustment and colour-matching; if a sample of steel has been left in a colouring bath for too long, the previous colour or shade to that produced may be obtained without the cost of repolishing the sample.

The reversion of colour may be achieved by treating the steel with a boiling aqueous solution of sodium sulphate with sulphuric acid or of sodium hypophosphite or of sodium nitrate, the last named being preferred, for example by immersion.

The coloured coatings produced according to the invention 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 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, as described in our Application No. 10344/66 (Serial No. 1,122,172).

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 example by washing with warm detergent solution and rinsing with water, or by washing with a 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 concentrated solutions of chromium trioxide 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, such as one made of polythene or polypropylene. Such a tank may still be attacked by hot chromic acid solution 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 tank in a water bath. The use of a water bath serves to reduce mounting stresses in the tank, and provides a ready temperature control of the contents of the tank, by control of the temperature of the water bath.

WHAT WE CLAIM IS:—

1. A process in which nickel-containing

stainless steel is coloured by immersing the steel in an aqueous solution containing chromium trioxide, sulphuric acid and from 0.3 to 50 g/l of manganous sulphate.

2. A process according to claim 1 in which the solution contains from 4 to 5 g/l of manganous sulphate.

3. A process according to claim 1 or claim 2 in which the solution contains from 50 to 1000 g/l of chromium trioxide and sufficient sulphuric acid to make the ratio of the weights of chromium trioxide to sulphate ion added as sulphuric acid between 100:1 and 1:1.

4. A process according to any one of claims 1 to 3 in which the solution contains from 520 to 580 g/l of chromium trioxide.

5. A process according to claim 4 in which the coloured steel is subsequently heated in air at from 300 to 700°C.

6. A process according to claim 1 in which the coloured steel is subsequently treated with a boiling aqueous solution of sodium sulphite with sulphuric acid or of sodium hypophosphite or of sodium nitrate.

7. A process according to claim 1 substantially as described with reference to Example 1 or Example 2 herein.

8. Stainless steel coloured by a process according to any one of claims 1 to 7.

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