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(54) TREATMENT OF CHROMIUM ALLOYS

(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 colouring of stainless steel and other corrosion-resistant chromium-containing alloys having a base of one or more of iron, cobalt and nickel by simple immersion in aqueous solutions of chromic acid and sulphuric acid with or without other additions such as manganous sulphate, for example as described and claimed in our U.K. Specifications Nos. 1,122,172 and 1,122,173. In these processes different colours are successively produced on the metal surface as the process continues, the range of colours depending on the composition of the alloy. Thus with austenitic nickel-chromium steels and ferritic chromium steels the range of colours is typically blue-gold-magenta-green, while with martensitic steels only a limited range of dark colours is obtained.

Whatever the colour range, it is found in practice that it is difficult to produce a given colour reproducibly under any given conditions, since not only does the colour change with the duration of the immersion of the metal in the solution but also the time for any given colour to be produced is found to vary under apparently unchanged conditions. Owing to the deep colouration of the colouring solutions themselves, visual control of the colouring process is impractical.

We have now found that the process can

be controlled so as to obtain a desired colour reproducibly by making use of the potential difference between the surface of the metal being coated and a reference electrode. This potential difference will be referred to for convenience as the potential of the metal.

More particularly, we have found that after the metal is immersed in the colouring solution the metal becomes increasingly electropositive, so that the potential of the metal, when measured against a less electropositive reference electrode such as a saturated calomel electrode or a mercurous sulphate electrode, begins to rise. Colouring does not however begin at once, but only after a period of time that may be from a few minutes to half an hour or more and seems to be of the nature of an induction period. Immediately before the film that is responsible for the appearance of colour begins to form on the metal surface, the potential or the rate of change of potential with time passes through a minimum. The potential at which this occurs will be referred to for convenience as the inflexion potential, since a graph of the potential of the metal against time generally exhibits a point of inflexion at this point. In many cases the rate of change of potential falls to zero and the potential may even remain constant for several minutes, giving a plateau on the potential-time curve.

As colouring proceeds through the range of colours characteristic of the metal being coloured, the potential continues to rise, reaching a maximum, referred to for convenience as the finish potential, when the colouring process is complete. The potential then falls a few millivolts to a substan-



tially constant value. If the metal is allowed to remain in the solution until this point is reached, it is found that the surface film has been degraded and become powdery and severe corrosion of the metal surface has occurred. For stainless steel the difference between the inflexion and finish potentials is generally between 25 and 35 millivolts.

Three typical curves showing the variation with time of the potential of three specimens of 18% Cr-8% Ni stainless steel, measured against a saturated calomel electrode, are given in Figure 1 of the drawings. Curve 1 relates to a specimen that has been electropolished before immersion, Curve 2 to a specimen that had been exposed to the atmosphere and Curve 3 to a specimen that had been thermally oxidised. Each of the three curves exhibits a minimum (A_1) or a point of inflexion (A_2, A_3) and a maximum (B_1, B_2, B_3). The inflexion potential is defined by the minimum (A_1) in Curve 1 and the point of inflexion (A_2, A_3) in Curves 2 and 3. Although the shape of the curves differs, and the values of the inflexion potential and finish potential with respect to the reference electrode may vary, the difference between the values of the inflexion potential and the finish potential is the same for each specimen. Between the inflexion potential and the finish potential the potential of the metal becomes progressively more positive as the colouring proceeds, and for a given combination of metal, colouring solution and temperature the rise in potential from the inflexion potential to the appearance of any given colour is constant.

Making use of these discoveries, according to the invention, in any given system we first determine the change in potential from the inflexion potential to the formation of the desired colour using a test specimen of the metal to be coated. Thereafter during the coating of further specimens their potential is monitored, and they are removed from the solution when this predetermined potential change has occurred.

The reference electrode may be a calomel electrode or any well known standard reference electrode with a bridge that is chemically stable in contact with the colouring solution such as a mercury/mercurous sulphate/5 Molar sulphuric acid system, but for simplicity we prefer to use a reference electrode consisting of a piece of platinum sheet immersed in the colouring solution. Less preferably the electrode may be of titanium. A portion of the metal being coloured that has passed the finish potential and achieved a stable potential may also be conveniently used as a reference electrode, although such electrodes are subject to potential variations of about 1 millivolt and to severe corrosion.

It will be appreciated that although the potential of stainless steel is more positive than that of a saturated calomel electrode, the potential of a platinum electrode is about 150 millivolts more positive than that of stainless steel, so that when such a reference electrode is used the potential of the metal as defined above will decrease as the metal becomes more positive, and the curves shown in Figure 1 will be inverted. Whatever reference electrode is used, it is extremely important in measuring the potential difference between the reference electrode and the specimen being coloured to use a voltmeter of such high impedance, e.g. in excess of $10^{10} \Omega$, that there is negligible current flow, since even a small current affects the colour of the film being formed on the metal.

An example of the use of the invention to control the colouring of stainless steel will now be given.

A specimen consisting of a sheet of Type 304 stainless steel was immersed in an aqueous solution containing 250 g/l chromic acid, calculated as CrO_3 , and 500 g/l of sulphuric acid at a temperature of 70°C . The potential difference between the specimen and a platinum reference electrode immersed in the solution was measured on a digital voltmeter of high impedance as the colouring process continued. The observed potential differences were plotted against time to give the curve shown in Figure 2 of the drawings. As mentioned above, this is inverted in relation to Figure 1, and it clearly exhibits the inflexion potential at A and the finish potential at B.

At the same time the colours produced on the stainless steel surface were observed, and these are also indicated on the drawing. It will be seen that at a potential from 6 to 8 mV below the point A a range of blue colours is produced, from 11 to 14 mV a range of gold colours, at 15 mV magenta and 17 mV peacock green.

On replacing the first piece of steel by another similar specimen and immersing it until the indicated potential changes from the level of point A had taken place, it was found that the colours produced were those predicted, though the actual potential difference between the metal surface and the reference electrode corresponding to the point A was not exactly the same in the two cases.

The shape of the graph does not depend on the reference electrode, but with a change of electrode the whole curve may move bodily up or down the ordinate scale, or may be inverted as explained above, though the potential change from the level of the point A for the production of a given colour remains the same. Small changes in the composition and operating temperature of a

5 solution such as may occur in its day to day use have little or no effect on the potential change associated with a given colour, but the shape of the curve may vary considerably with such changes.

10 Colours obtained near the end of the colour range, i.e. close to the finish potential (point B), suffer from poorer reproducibility since the colour changes more rapidly as the potential above the inflexion potential (point A) increases. Furthermore the film begins to break up as the finish potential is approached, with the result that an inferior product is obtained.

15 In practising the invention it is convenient to record the potential of the metal continuously by means of a chart recorder connected to the voltmeter. The inflexion potential may then be determined visually from the trace on the chart. The inflexion potential may also be determined directly by means of a suitable rate-of-change voltmeter.

25 If the inflexion in the change of potential with time is indistinct, it may be advantageous to subject the metal to a treatment to remove the surface film, for example an anodic treatment in an acid electrolyte, for example dilute sulphuric acid, before commencing the colouring process.

30 Generally speaking, chromium-containing metals which can be coloured in accordance with the present invention include both chromium-containing stainless steels and corrosion-resistant, chromium-containing alloys other than steel on which films can be formed and then satisfactorily cathodically hardened. These alloys usually contain at least about 12.5% by weight of chromium and 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. For purposes of this specification and claims, stainless steels include iron-base alloys containing greater than about 11% and up to about 30% chromium.

55 If the electrical connection between the metal being coloured and the voltmeter is exposed to the colouring solution it must of

course be of the same position as the metal being coloured, and neither it nor the jig holding the specimen must bear a colour film produced by the process, as this would falsify the potential observed. If several articles of the same material and surface condition are being coloured simultaneously in one bath, they may be connected with clean conductors of the same composition, e.g. a common jig, and it is then only necessary to monitor the potential of the whole assembly of articles.

In some freshly-prepared chromic-acid/sulphuric acid colouring solutions it has been found that the relationship between potential and time may not be so smooth as in the accompanying drawings. In carrying out the invention it is therefore desirable to 'run-in' the colouring bath by colouring scrap metal specimens or by direct current electrolysis until a smooth curve is obtained.

WHAT WE CLAIM IS:—

1. A method of controlling the colouring of the surface of a chromium-containing alloy by immersion in an aqueous solution of chromic and sulphuric acids which comprises monitoring the potential difference between the surface of the alloy being coloured and a reference electrode and removing the alloy from the solution when this potential difference has changed from the value at which film formation begins by a predetermined amount associated with the desired colour.

2. A method according to claim 1 in which the reference electrode consists of a platinum or titanium electrode immersed in the colouring solution.

3. A method according to claim 1 or claim 2 applied to the colouring of chromium-containing stainless steel.

4. A method according to any preceding claim in which the potential difference between the surface of the alloy and the reference electrode is continuously recorded.

5. A method according to claim 1 substantially as herein described by way of example.

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anodic treatment in an acid electrolyte, for
30 example dilute sulphuric acid, before commencing
the colouring process.

Generally speaking, chromium-containing
metals which can be coloured in accordance
with the present invention include both
chromium-containing stainless steels and
35 corrosion-resistant, chromium-containing
alloys other than steel on which films can
be formed and then satisfactorily cathodically
hardened. These alloys usually contain
at least about 12.5% by weight of
40 chromium and 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
45 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. For purposes of this specification
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iron-base alloys containing greater than
about 11% and up to about 30% chromium.

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e.g. a common jig, and it is then only
65 necessary to monitor the potential of the
whole assembly of articles.

In some freshly-prepared chromic-acid/
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of chromic and sulphuric acids which comprises
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the surface of the alloy being coloured and a
reference electrode and removing the alloy from
the solution when this potential difference has
changed from the value at which film formation
begins by a predetermined amount associated
85 with the desired colour.

2. A method according to claim 1 in
which the reference electrode consists of a
platinum or titanium electrode immersed in
the colouring solution.

3. A method according to claim 1 or
claim 2 applied to the colouring of
chromium-containing stainless steel.

4. A method according to any preceding
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