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Skedgell et al.

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[54] **REPRODUCIBILITY OF COLOR IN COLORING STAINLESS STEEL**

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[51] **Int. Cl.** **C23f 1/26**
[58] **Field of Search** ..... 148/6.2, 6.14; 204/195 F; 324/29, 30 R

[56] **References Cited**

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Primary Examiner—Ralph S. Kendall

[57] **ABSTRACT**

A process of coloring chromium-containing metal in a chromic acid bath wherein the potential of the surface of the metal being colored is monitored against a standard electrode and the metal is removed from the bath when a predetermined change in potential has occurred starting from an inflection point on a potential-time curve.

5 Claims, 2 Drawing Figures

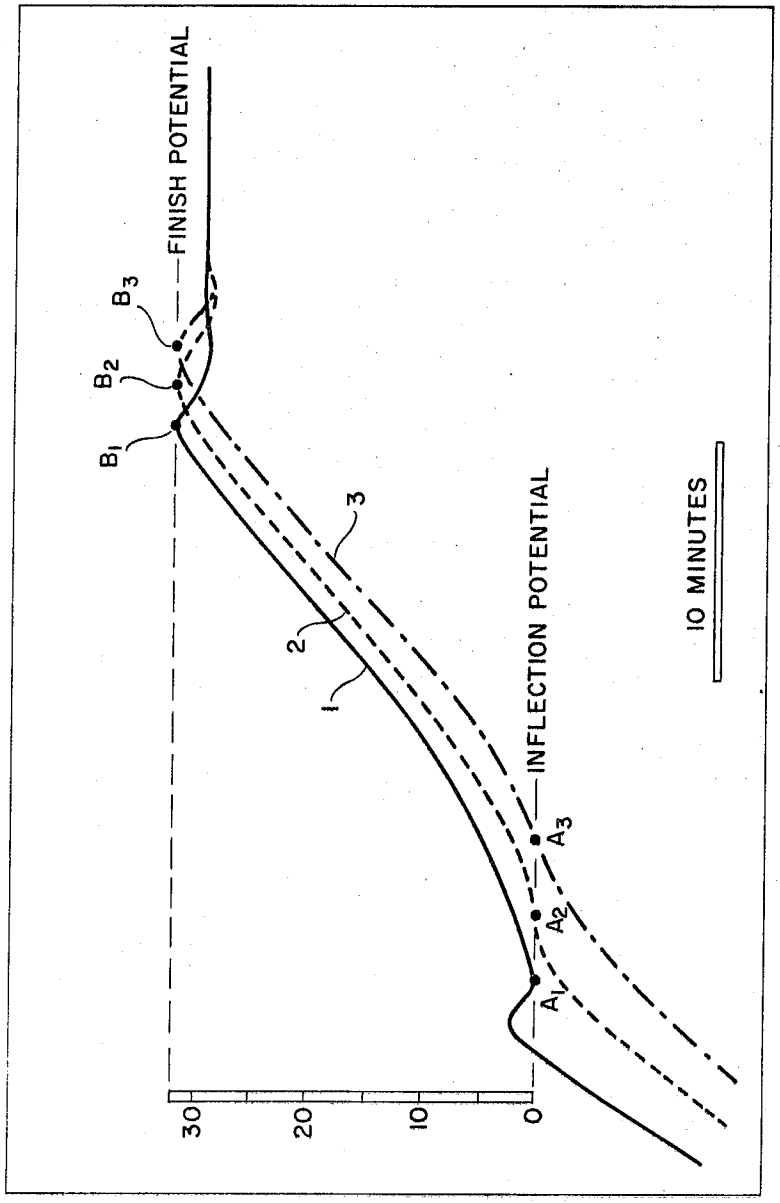

FINISH POTENTIAL
B3
B2
B1
3
2
1
INFLECTION POTENTIAL
A3
A2
A1
10 MINUTES
TIME
30
20
10
0
POTENTIAL OF SPECIMEN (M.V.)

Fig. 1

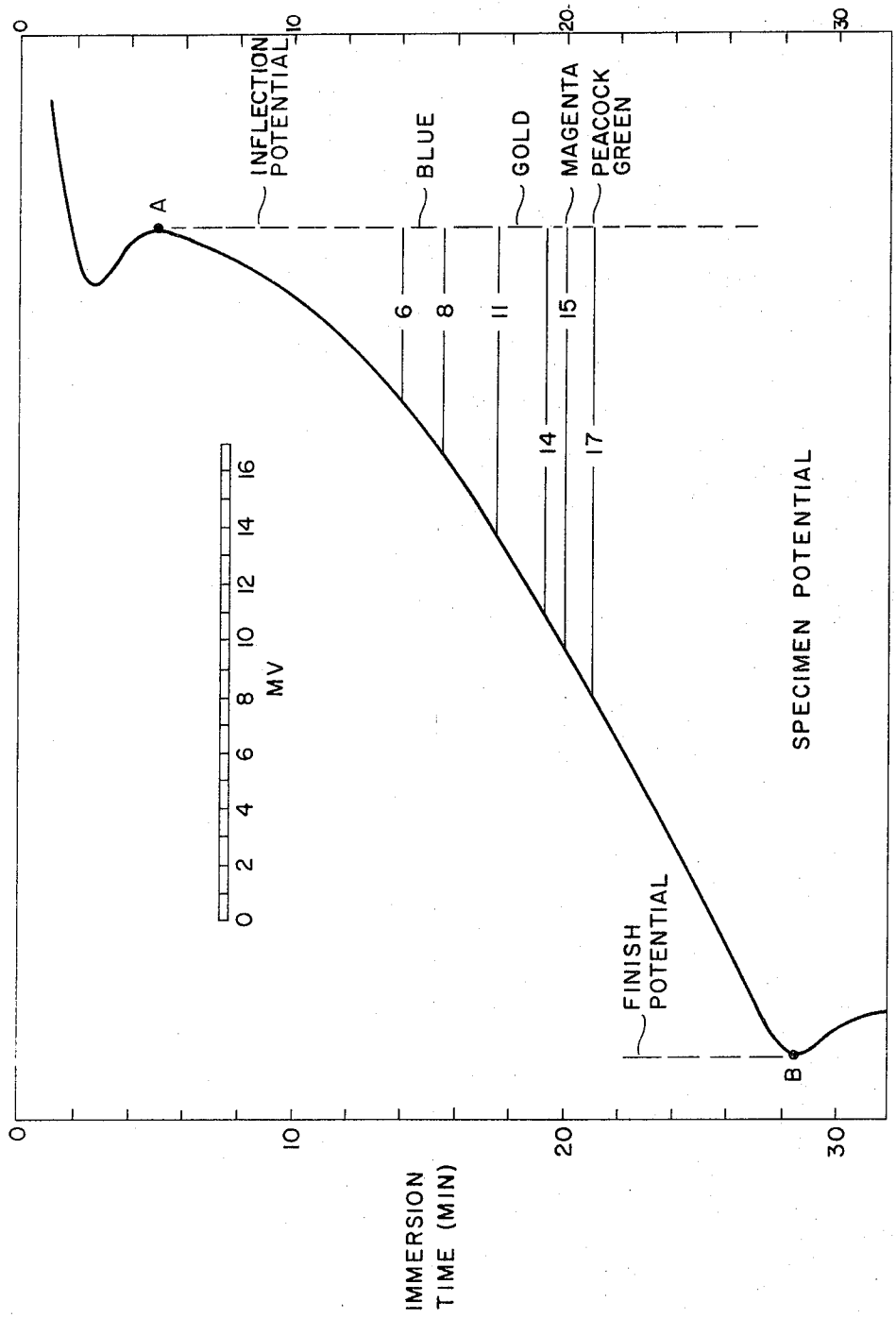

INFLECTION POTENTIAL
BLUE
GOLD
MAGENTA
PEACOCK GREEN
A
B
6
8
11
14
15
17
MV
0 2 4 6 8 10 12 14 16
SPECIMEN POTENTIAL
FINISH POTENTIAL
0
10
20
30
IMMERSION TIME (MIN)

Fig. 2

REPRODUCIBILITY OF COLOR IN COLORING STAINLESS STEEL

This invention relates to the coloring of stainless steel and other corrosion-resistant chromium-containing alloys having a base of one or more of iron, cobalt and nickel and, more particularly, to the control of coloring of these alloys when colored by simple immersion in aqueous solutions of chromic acid and sulfuric acid with or without other additions such as manganese sulfate, for example, as described and claimed in U.K. Pat. Nos. 1,122,172 and 1,122,173.

In the patented processes different colors are successively produced on the metal surface as the process continues, the range of colors depending on the composition of the alloy. Thus with austenitic nickel-chromium steels and ferritic chromium steels the range of colors is typically blue-gold-magenta-green, while with martensitic steels only a limited range of dark colors is obtained.

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

We have now found that the coloring process can be controlled so as to obtain a desired color reproducibly by making use of the potential difference between the surface of the metal being colored and a reference electrode. This potential difference will be referred to for convenience as the potential of the metal.

It is an object of the present invention to provide a process of coloring chromium-containing alloy which process is conveniently controlled to provide consistently colored products.

Other objects and advantages will become apparent from the following description taken in conjunction with the drawing in which:

FIGS. 1 and 2 are graphs interrelating potential of a chromium-containing metal being colored and time as experienced in carrying out the process of the present invention.

More particularly, we have found that after the metal is immersed in the coloring 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 sulfate electrode, begins to rise. Coloring 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 or coating that is responsible for the appearance of color begins to form on the metal surface, 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 inflection potential, since a graph of the potential of the metal against time exhibits a point of inflection 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 coloring proceeds through the range of colors characteristic of the metal being colored, the potential continues to rise, reaching a maximum, referred to for convenience as the finish potential, when the coloring process is complete. The potential then falls a few millivolts to a substantially 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 inflection 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 percent Cr — 8 percent Ni stainless steel, measured against a saturated calomel electrode, are given in FIG. 1 of the drawing. Curve 1 relates to a specimen that had 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 oxidized. Each of the three curves exhibits a point of inflection (A_1, A_2, A_3) and a maximum (B_1, B_2, B_3). Where, as in Curve 1, there are two points of inflection before coloring begins, the second defines the inflection potential. Although the shapes of the curves differ and the values of the inflection potential and finish potential with respect to the reference electrode may vary, the difference between values of the inflection potential and the finish potential is the same for each specimen. Between the inflection potential and the finish potential, the potential of the metal becomes progressively more positive as the coloring proceeds, and for a given combination of metal, coloring solution and temperature the rise in potential from the inflection potential to the appearance of any given color is constant.

Making use of these discoveries, according to the invention, in any given system we first determine the change in potential from the inflection potential to the formation of the desired color 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 coloring solution such as a mercury/mercurous sulfate/5 Molar sulfuric acid system, but for simplicity we prefer to use a reference electrode consisting of a piece of platinum sheet immersed in the coloring solution. Less preferably, the electrode may be of titanium. A portion of the metal being colored 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 FIG. 1 will be inverted. Whatever reference electrode is used, it is extremely important in measuring the potential difference between the refer-

ence electrode and the specimen being colored 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 color of the film being formed on the metal.

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

A specimen consisting of a sheet of Type 304 18 percent Cr — 8 percent Ni stainless steel was immersed in an aqueous solution containing 250 grams per liter (g/l) chromic acid, calculated as CrO_3 and 500 g/l of sulfuric 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 coloring process continued. The observed potential differences were plotted against time to give the curve shown in FIG. 2 of the drawings. As mentioned above, this is inverted in relation to FIG. 1, and it clearly exhibits the inflection potential at A and the finish potential at B.

At the same time the colors 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 millivolts below the point A a range of blue colors is produced, from 11 to 14 millivolts a range of gold colors, at 15 millivolts magenta and 17 millivolts 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 colors 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 or increment (either positive or negative) from the level of the point A for the production of a given color remains the same. Small changes in the composition and operating temperature of a solution such as may occur in its day-to-day use have little or no effect on the potential change associated with a given color, but the shape of the curve may vary considerably with such changes.

Colors obtained near the end of the color range, i.e., close to the finish potential (point B), suffer from poorer reproducibility since the color changes rapidly as a function of the potential above the inflection potential (point A). Furthermore, the film begins to break up as the finish potential is approached, with the result that the inferior product is obtained.

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

It may sometimes happen that the inflection in the change of potential with time is too indistinct for accurate measurement. It may then be advantageous to subject the metal to a treatment to remove the oxide film, for example, by an anodic treatment in an acid electrolyte before commencing the coloring process.

Generally speaking, chromium-containing metals which can be colored 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 percent by weight of chromium and include iron-based nickel-chromium-molybdenum alloys such as an alloy containing 37 percent nickel, 18 percent chromium, 5 percent molybdenum, 1.2 percent titanium and 1.2 percent aluminum; cobalt-based alloys such as that containing 21 percent chromium, 21 percent nickel and 13 percent molybdenum; and nickel-chromium alloys, such as an alloy containing 30 percent chromium and 1 percent titanium, the remainder being nickel. For purposes of this specification and claims, stainless steels include iron-base alloys containing greater than about 11 percent and up to about 30 percent chromium.

If the electrical connection between the metal being coated and the voltmeter is exposed to the coloring solution, it must, of course, be of the same composition as the metal being coated, and neither it nor the jig holding the specimen must bear a color film produced by the process, as this would falsify the potential observed. If several articles of the same material and surface condition are being colored 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/sulfuric acid coloring solutions it has been found that the relationship between potential and time may not be so smooth as in the accompanying drawing. In carrying out the invention it is therefore desirable to "run-in" the coloring bath by coloring scrap metal specimens or by direct current electrolysis until a smooth curve is obtained.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

We claim:

1. In a process for coating chromium-containing alloy with coatings ranging from colorless through a series of colors comprising treating said alloy in an aqueous chromic acid solution for a time until a desired surface condition is realized, the improvement comprising measuring in said solution the potential of the surface of said alloy against a standard electrode and removing said alloy from said solution when the difference between the inflection potential of said alloy surface and the potential measured thereafter against said standard electrode equals a predetermined potential change associated with said desired surface condition.

2. A process as in claim 1 wherein the chromium-containing alloy is stainless steel.

3. A process as in claim 1 wherein the standard electrode consists of platinum or titanium immersed in the aqueous chromic acid solution.

4. A process as in claim 1 wherein the predetermined potential change is less than about 35 millivolts.

5. A process as in claim 4 wherein the predetermined potential change is within the range of about 6 to about 17 millivolts.

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