United States Patent Office 3,093,556 Patented June 11, 1963



3,093,556

# ELECTRO-DEPOSITING STAINLESS STEEL COATINGS ON METAL SURFACES

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No Drawing. Filed June 13, 1961, Ser. No. 116,699
6 Claims. (Cl. 204—43)

This invention relates to the electro-deposition of the stainless steel coatings on metal surfaces and is particularly concerned with the provision of a method of and solutions for electro-depositing coatings of alloys consisting of iron, chromium and nickel on certain metal surfaces.

Before stating the principal objects of the invention and describing its details it will be helpful to review briefly certain practices of the prior art. For instance, it is well known that enhanced corrosion resistance may be imparted to metal surfaces by electro-depositing on the surfaces either chromium or nickel or alloys of iron and chromium or of iron and nickel. However, where it has been desired to obtain a coating which includes both chromium and nickel in addition to iron, i.e., an alloy of all three of these metals, it has been customary to hot roll a sheet of stainless steel onto the surface of the metal to be protected or to spray on the surface molten stainless steel by means of compressed air. The spraying technique has not found widespread industrial application due to certain difficulties and high costs involved in such an operation. As for the rolling procedure, it is obvious that it has to be restricted to flat surfaces which, of course, means that irregularly shaped articles cannot be subjected to such a process. Beyond this, the rolling method is subject to a further disadvantage incident to the fact that when cutting the sheet, the edges so exposed are uncoated so that the base metal is subject to corrosive environments at such edges.

In addition, the art also has attempted to apply coatings which have the approximate analysis of stainless steel by using a chromium-nickel deposition upon ferrous surfaces followed by a heat fusion treatment, but such technique has not been successful in obtaining the desired stainless steel coating.

With the foregoing in mind, the principal object of the present invention resides in the provision of a process by means of which iron, chromium and nickel may be electrodeposited simultaneously upon a base metal to produce thereon a stainless steel alloy of all three of these metals.

The present invention is based upon the discovery that iron, chromium and nickel can be deposited simultaneously from an electrolytic solution containing the ions of all three of these metals to yield a coating upon a base metal which coating contains an alloy of the said metals and, under conditions to be described below, that the said coating can be given the approximate analysis of the so-called stainless steels. The metal to be coated is made the cathode and the electrolytic solution must contain, as essential coating producing ingredients, from 0.2 mol/liter to saturation of each of the ions of iron, chromium and nickel and at least 1.0 mol/liter of urea. For best results the coating solution should be operated at temperatures ranging from 30° to 80° C. and at a pH from about 1.5



to about 3.5 and that a current density of from 0.645 to 2.148 amps./in.$^2$ should be employed.

As stated, the metal to be coated must serve as cathode in the electrolytic solution and we have found that coatings of this invention can be applied to metals from the group which consists of iron, copper, zinc, nickel and alloys of each wherein the particular metal constitutes the principal ingredient.

The anode employed may be, and preferably is, of the conventional type—for example, one of platinum or graphite composition. However, if desired, stainless steel anodes may be employed and, more particularly, stainless steels of what are known as the SAE 304 and 305 types. Where such stainless steel anodes are used it should be noted at this time that the electrolytic solution should include chloride ion in order to facilitate dissolution of these anodes as will further appear.

The concentration of the iron, chromium and nickel ions must each be at least 0.2 mol/liter calculated as the respective metal ion and these ions are preferably introduced into the solution in the form of their chloride or sulphate salts. The concentration of these ions in the solution is limited only by the solubility of the respective salts in a particular coating bath.

The type of chloride or sulphate salt which may be utilized is not critical but, in the interests of economy, it is preferred to employ hydrated salts of the respective metals. Where the anode employed consists of SAE type 304 or 305 stainless steel it is unnecessary to add additional salts of the respective metals so long as there is enough chloride ion in the electrolyte to effect dissolution of sufficient of the anode to yield at least 0.2 mol/liter of each of the respective metal ions.

In addition to the metal ions as specified above the electrolytic bath must also include urea in an amount which is not less than 1.0 mol/liter and preferably should lie between 1.0 and 4.0 mols/liter. Where less than 1.0 mol/liter of urea is employed chromium deposition is impaired so that only very small amounts of this metal may be deposited in relation to the total coating. On the other hand, if more than 4.0 mols of urea per liter are employed, chromium deposits at an increasingly rapid rate at the expense of the nickel constituent so that only very small quantities of nickel would be plated on the piece.

Dissolution of both the metal salts which may be employed as well as of the urea may require the addition to the electrolytic solution of free acid in the form of hydrochloric or sulfuric acids in order to provide the operable pH range which is required, namely between 1.5 and 3.5. On the other hand, if the pH of the solution as prepared is less than 1.5, small amounts of ammonium hydroxide may be added to raise the pH to within the level desired. A pH below 1.5 is undesirable inasmuch as it results in decreased chromium content in the coating as well as decrease in the total coating weight and an increase in pitting of the coated articles. A pH above 3.5 tends to cause decrease in the percent of yield based on current efficiency for both chromium and iron and a rapid increase in the nickel concentration of the alloy which is deposited.

In order to demonstrate the effect of variations in the pH of the electrolytic bath reference is made to the following examples. In the first place a series of baths were

prepared all of which contained per liter the following ingredients:

| | Mols |
|---|---|
| $Cr_2(SO_4)_3 \cdot 15H_2O$ | 0.4 |
| $FeSO_4 \cdot 7H_2O$ | 0.2 |
| $NiSO_4 \cdot 7H_2O$ | 0.4 |
| Urea | 3.0 |
| $H_3BO_3$ | 0.4 |

Baths of said composition were operated at 50° C. and copper was used as the cathode with a current density of 1.716 amps./in.² for a 5-minute period of deposition. Table I below sets forth in tabular form the results of the tests which were made:

*Table I*

| pH | Grams alloy | Percent metal in alloy | | | Percent current yield on— | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Fe | Ni | Alloy | Cr | Fe | Ni |
| 0.5 | 0.0028 | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
| 1.1 | 0.0202 | 0 | 82.0 | 18.0 | 5.73 | 1.95 | 4.75 | 0.98 |
| 1.5 | 0.0504 | 8.4 | 76.8 | 14.6 | 15.11 | 3.71 | 11.1 | 2.00 |
| 1.7 | 0.0610 | 13.1 | 74.1 | 12.8 | 18.86 | 3.71 | 13.0 | 2.13 |
| 2.1 | 0.0704 | 15.3 | 72.4 | 12.2 | 22.04 | 5.01 | 14.7 | 2.35 |
| 2.3 | 0.0726 | 17.1 | 70.6 | 12.3 | 22.97 | 5.75 | 14.8 | 2.44 |
| 3.0 | 0.0684 | 14.7 | 71.3 | 14.0 | 21.33 | 4.64 | 14.1 | 2.63 |
| 3.5 | 0.0622 | 6.4 | 75.5 | 18.0 | 18.45 | 1.85 | 13.5 | 3.07 |

[1] Not determined

The current yields were computed for the individual metals as well as for the alloy, after each of the metals in the coating had been analytically determined for the respective current density and duration of the electrolysis. The computation was based on the following formulas:

The electrochemical equivalent weight W in g./ah. at a 100% current yield is determined by the formula:

$$W=\frac{w_1 \cdot w_2 \cdot w_3}{f_1 w_2 w_3 + f_2 w_1 w_3 + f_3 w_1 w_2}$$

in which $w_1$, $w_2$, and $w_3$ designate the electrochemical equivalents of the three metals, and $f_1$, $f_2$, and $f_3$ designate the proportional weights of these three metals, the sum of $f_1$, $f_2$, and $f_3$ amounting to 1.

The current yield of the alloy S is determined by the formula:

$$S=\frac{\text{Weight of alloys} \times 100\ (f_1 w_2 w_3 + f_2 w_1 w_3 + f_3 w_1 w_2)}{\text{Current density} \times \text{time in } h \times w_1 \cdot w_2 \cdot w_3}$$

where $h$ represents hours.

The thickness of the percipitates ($d$) is determined by the formula:

$$d=\frac{\left(\text{Weight Fe} \times \frac{1}{7.87} + \text{weight Cr} \times \frac{1}{7.19} + \text{weight Ni} \times \frac{1}{8.9}\right)}{\text{Area in cm.}^2}$$

in which the fractions signify the reciprocal specific weights of the three metals.

From the above Table I it will be observed that under the conditions given a pH between 2.1 and 2.3 yielded alloy coatings having the approximate analyses of SAE stainless steels known as types 305, 316 and 347. For example, stainless steel type 305 generally contains from 17 to 19% chromium and 10 to 13% nickel with the balance iron. Type 316 contains from 16 to 18% chromium and 10 to 14% nickel with the balance iron and type 347 usually has a composition of approximately 17 to 19% chromium and 9 to 12% nickel with the balance iron. Of course, certain very small percentages of other ingredients such as silicon, carbon and manganese are often present in such stainless steels but these can be ignored insofar as the present invention is concerned.

As noted hereinabove, the deposition of chromium-nickel-iron alloys must be effected by employing a current density of from about 0.645 to 2.148 amps./in.². In the particular example of Table I, as stated, 1.716 amps./in.² were employed. Where current densities greater than about 2.148 amps./in.² are utilized the deposited alloy tends to develop fissures and cracks and sometimes burning of the base metal results. On the other hand, at a current density below about 0.645 amp./in.² the chromium content of the deposited coating tends to fall off to a low level as also does the total alloy yield.

To illustrate the effect of changes in current density another series of tests were run the results of which are tabulated in Table II below. The solution employed was of the same compression as that specified above for use in Table I and the conditions of operation were essentially the same with the pH being maintained at approximately 2.1 throughout the tests. The factor which was changed was the current density as shown by the table. The cathode employed was again copper.

*Table II*

| Current density, amps./in.² | Grams alloy | Percent metal in alloy | | | Percent current yield on— | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Fe | Ni | Alloy | Cr | Fe | Ni |
| 0.212 | 0.0038 | (1) | (1) | (1) | (1) | (1) | (1) | (1) |
| 0.426 | 0.0121 | 7.6 | 72.4 | 19.9 | 14.4 | 1.67 | 10.1 | 2.63 |
| 0.858 | 0.0302 | 9.4 | 72.0 | 18.5 | 18.2 | 2.60 | 12.5 | 3.07 |
| 1.290 | 0.0521 | 12.4 | 72.3 | 15.2 | 21.3 | 3.96 | 14.5 | 2.90 |
| 1.716 | 0.0720 | 15.3 | 72.4 | 12.3 | 22.5 | 5.10 | 15.0 | 2.41 |
| 2.148 | 0.1101 | 16.9 | 70.0 | 13.1 | 27.8 | 6.90 | 17.8 | 3.15 |
| 2.360 | 0.1074 | 17.3 | 70.0 | 12.7 | 24.7 | 6.24 | 15.8 | 2.72 |

[1] Not determined.

From the above table it may be observed that stainless steels of types 305, 316 and 347 are more closely approximated under the conditions of the bath where current densities of from about 1.716 to about 2.148 are employed.

In order to illustrate the effect of variations in the temperature of the bath still another series of tests were undertaken and these are reported in Table III below. In these tests the bath was the same as the bath used for Tables I and II and copper cathodes were again employed. The pH of the electrolytic solution was maintained at approximately 2.1 and the current density employed was 1.716 amps./in.². The temperatures, however, varied widely as shown.

*Table III*

| Temperature, ° C. | Grams alloy | Percent metal in alloy | | | Percent current yield on— | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Fe | Ni | Alloy | Cr | Fe | Ni |
| 30 | 0.0667 | 27.1 | 69.1 | 3.7 | 22.3 | 8.4 | 13.3 | 0.66 |
| 40 | 0.0675 | 20.1 | 71.8 | 7.9 | 21.7 | 6.3 | 13.9 | 1.48 |
| 50 | 0.0710 | 15.3 | 72.4 | 12.3 | 22.2 | 5.1 | 14.8 | 2.38 |
| 60 | 0.0786 | 7.9 | 73.9 | 18.1 | 23.3 | 2.8 | 16.6 | 3.89 |
| 70 | 0.0850 | 4.8 | 70.8 | 24.4 | 24.9 | 1.9 | 17.3 | 5.67 |
| 80 | 0.0966 | 0.9 | 69.7 | 29.3 | 27.5 | 0.4 | 19.4 | 7.75 |

Analysis of Table III shows that lower temperatures favor chromium deposition at the expense of nickel and this is reflected both in the actual weight of the metals deposited and in the percent current yields based on the respective metals. Furthermore, the current yield based on iron will be observed to increase gradually with increased temperatures. The total alloy deposited increases with increase in temperature and the alloy deposits which approximate the analysis of stainless steels 305, 316 and

347 are obtained where the temperature ranges from about 40° to 50° C. under the conditions of this test.

Insofar as time of treatment is concerned, it has been found that the duration of the electroplating reaction has essentially no marked influence upon the composition of the alloy except that prolonged electrolysis under otherwise constant conditions tends to cause a decrease in the current yield and also tends to dull the finish of the plated coating. To demonstrate this is a series of tests were run which are reported in Table IV below, the solutions employed being the same as those heretofore used in connection with Tables I, II and III. The cathodes were copper as in the previous tests while the temperature was held at approximately 50° C. and the pH at approximately 2.1.

*Table IV*

| Current density, amps./in.² | Time, min. | Grams alloy | Percent metal in alloy | | | Percent current yield on— | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cr | Fe | Ni | Alloy | Cr | Fe | Ni |
| 1.716 | 2 | 0.0284 | 15.1 | 73.1 | 11.8 | 22.2 | 5.0 | 14.8 | 2.4 |
| 1.716 | 5 | 0.0710 | 15.3 | 72.4 | 12.3 | 22.2 | 5.1 | 14.8 | 2.4 |
| 1.716 | 10 | 0.1430 | 15.3 | 72.5 | 12.2 | 22.2 | 5.1 | 14.8 | 2.4 |
| 1.716 | 15 | 0.2100 | 15.3 | 72.7 | 12.2 | 21.9 | 5.0 | 14.6 | 2.4 |
| 1.716 | 20 | 0.2370 | 15.3 | 72.7 | 12.3 | 18.6 | 4.2 | 12.4 | 2.0 |
| 1.290 | 20 | 0.2100 | 12.2 | 72.3 | 15.2 | 21.5 | 4.0 | 14.6 | 2.9 |

The decrease in current density reported in the last line of Table IV served to improve the brightness of the deposited alloy and also that such current density decreased the chromium and increased the nickel constituents of the deposited alloy.

Insofar as the base metal which can be coated is concerned, the process of this invention is applicable to metals from the group consisting of copper, iron, nickel, zinc and alloys of each wherein the particular metal constitutes the principal ingredient. In order to illustrate the character of the alloys deposited where the cathode is chosen from these metals, there is presented below Table V. The solutions employed in carrying out the tests of Table V were the same as those used for the previous tables with the pH at 2.1, the current density at 1.716 amps./in.², the temperature at 50° C. and the duration of the operation being 5 minutes.

*Table V*

| Base metal | Grams alloy | Percent metal in alloy | | | Current yield, percent | | | |
|---|---|---|---|---|---|---|---|---|
| | | Cr | Fe | Ni | Alloy | Cr | Fe | Ni |
| Copper | 0.0712 | 15.33 | 72.4 | 12.26 | 22.28 | 5.05 | 14.85 | 2.38 |
| Brass | 0.0660 | 15.30 | 72.4 | 12.27 | 20.66 | 4.68 | 13.76 | 2.21 |
| Nickel | 0.0780 | 15.27 | 72.3 | 12.30 | 24.42 | 5.52 | 16.26 | 2.63 |
| Zinc | 0.0870 | 15.28 | 71.7 | 12.28 | 27.24 | 6.17 | 18.13 | 2.93 |
| Iron | 0.0880 | 15.34 | 72.3 | 12.28 | 27.52 | 6.26 | 18.24 | 3.00 |

From the results tabulated in Table V it is shown that the alloy deposited, while varying in total weight with the cathode employed, remains essentially unchanged with respect to the constituents of the alloy deposited. The greatest yields of alloy were obtained when using zinc and iron as cathodes and the smallest yield resulted from the use of brass as the cathode.

In order to illustrate the effects of the process of the present invention in depositing a chromium-nickel-iron alloy on copper cathodes and also to demonstrate the effects of variations in operating conditions, there is presented below in Table VI a series of six specific test results which are presented merely by way of illustration and with no intention that they be construed as limitations on this disclosure.



*Table VI*

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Mols/liter of: | | | | | | |
| $Cr_2(SO_4)_3 \cdot 15H_2O$ | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| $FeSO_4 \cdot 7H_2O$ | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 | 0.2 |
| $NiSO_4 \cdot 7H_2O$ | 0.4 | 0.2 | 0.4 | 0.4 | 0.4 | 0.4 |
| $NiCl_2 \cdot 6H_2O$ | | 0.2 | | | | |
| Urea | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 | 2.0 |
| $H_3BO_3$ | | 0.4 | 0.4 | 0.4 | 0.4 | |
| Temperature, °C | 40 | 50 | 60 | 30 | 50 | 50 |
| pH | 2.1 | 2.1 | 2.15 | 2.1 | 2.1 | 2.2 |
| Current density, amps./in.² | 1.716 | 1.290 | 1.716 | 1.716 | 1.716 | 1.716 |
| Alloy analysis, percent: | | | | | | |
| Cr | 21.4 | 12.3 | 8.2 | 27.1 | 15.3 | 13.1 |
| Fe | 71.3 | 72.3 | 58.5 | 69.1 | 72.4 | 73.1 |
| Ni | 7.0 | 15.24 | 33.0 | 3.6 | 12.3 | 13.7 |
| Current efficiency, percent | 20 | 21.3 | 17.5 | 22.3 | 22.2 | 18.0 |

If desired, boric acid may be added to the electrolytic solutions used with this invention for the purpose of providing smoother and somewhat more homogeneous coatings of the 3-component alloy being deposited and where used the amount of boric acid should be between about 0.2 and 0.6 mol per liter.

It is also possible, if desired, to include brightening agents in the electro-plating solutions of this invention. For example, a bath similar to that of Example 6 in Table VI as noted above was operated with the inclusion of 40 drops of pyridine per liter, which brightened the alloy deposited and produced thereon a relatively high gloss which is desirable in certain operations.

It should also be noted, as is well known in the art of electro-deposition that, for certain applications, it may be desirable to subject the electro-plated article to a subsequent heat treatment in order to remove hydrogen which is adsorbed by the coating during the plating operation.

We claim:

1. The method of electro-depositing a stainless steel alloy coating consisting of chromium, nickel and iron on a metal surface, with chromium constituting from about 8.2% to about 27.1% of the deposit, nickel from about 3.6% to about 33% and iron the balance, the iron content being predominantly greater than either chromium or nickel and at least 58.5%; said method comprising using the metal to be coated as cathode in a plating bath consisting essentially of an aqueous solution of from 0.2 mol/liter to saturation of the sulfate salt of each of the metals in the alloy to be deposited and from 1 to 4 mols/liter of urea with the balance water; maintaining the temperature of the bath at from 30° C. to 80° C., the pH at from 1.5 to 3.5, and passing an electric current of from 0.645 to 2.148 amps./in.² therethrough between an anode and the said cathode.

2. The method of claim 1 wherein the bath also contains from 0.2 to 0.6 mol/liter of boric acid with the balance water.

3. The method of claim 1 wherein a stainless steel anode is employed and wherein the bath includes chloride ion in quantity sufficient to insure the dissolution of enough of said anode to maintain the content of said metal ions.

4. The method of claim 1 wherein the bath is maintained at a temperature of from 40° C. to 50° C., the pH at from 2.1 to 2.3 and the current density at from 1.716 to 2.148 amps./in.².

5. The method of claim 1 wherein the bath also contains from 0.2 to 0.6 mol/liter of boric acid and, further, wherein the bath is maintained at a temperature of from 40° C. to 50° C., the pH at from 2.1 to 2.3 and the current density at from 1.716 to 2.148 amps./in.².

6. As a new article, a metal piece chosen from the group consisting of iron, zinc, nickel, copper and alloys of each in which the metal constitutes the principal ingredient, said article carrying an electro-deposited, stain-

less steel, alloy coating having a composition as described in and produced according to the method of claim 1.

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