ELECTRODEPOSITION OF A CORROSION RESISTANT COATING

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No Drawing.

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3 Claims. (Cl. 284-44)

This application is a continuation-in-part of my copending application, Serial No. 11,450, filed February 29, 1960, and now abandoned.

This invention relates to corrosion resistant composite metallic articles and to high throwing power electrodeposition methods of producing said articles.

Considerable effort has been devoted to the production of corrosion resistant plated metallic articles and particularly corrosion resistant nickel plated articles. Nickel is especially suitable for corrosion prevention in that it forms coatings which are more or less of a permanent white appearance and possess a high degree of resistance to corrosion by natural waters, sea water and alkaline and salt solutions. Nickel coatings, however, are also subject to corrosion due to certain phenomena existing in the structure of the coating and in the relation existing between the various components of the coated article.

Corrosion of nickel and nickel-chromium plated articles is primarily due to two factors. One of these factors is the so-called initial porosity of the coating. The initial porosity may be defined as small pores which are present in the coating layer before any corrosion has taken place. This type of porosity may be minimized by (a) proper base preparation, (b) absence of insoluble matter in the plating solution, and (c) use of thicker deposits. For nickel deposits greater than 1 mil in thickness the initial porosity is usually very low.

The second factor causing corrosion is galvanic in nature and is usually associated with discontinuities at the surface of the coating. These discontinuities or areas of galvanic action can be due to cracks or pores in the chromium deposit or to particles of air borne dusts coating the surface. Due to moisture and the presence of various electrolytes therein, a galvanic cell is set up in the area of the discontinuity which gradually causes the nickel to be dissolved and a hole or pore to develop. The type of nickel and chromium coating and the atmosphere to which the coating is subjected will affect the rate of galvanic penetration. It is important to note that thickness is again an important factor. The heavier deposits have fewer initial pores and also a longer time is required for galvanic penetration to reach the substrate.

Therefore, in commercial operation every effort is made to use as thick a deposit as the limitations will permit. A proper thickness may be achieved either through the use of nickel alone or nickel used in conjunction with an undercoating metal such as copper. It has been found, however, that heavier deposits of copper under nickel are not always beneficial. Apparently, the copper next to steel or a zinc die casting or an aluminum substrate will frequently create a galvanic action, through pores which are present, which is greater than the nickel-substrate galvanic action.

It would appear that a heavy coating of nickel alone would provide maximum corrosion resistance. However, as mentioned above, even when obtained from nickel solutions such as, for instance, the method given in U.S. Patent No. 1,750,092, the preferred method, however, is that outlined by B. H. Priscott (Transactions of the Institute of Metal Finishing 36, 93-96 (1958-9)).
An example of a specific copper-nickel alloy bath which may be employed is as follows:

<table>
<thead>
<tr>
<th>Grams per liter</th>
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<tbody>
<tr>
<td>Sodium chloride</td>
</tr>
<tr>
<td>Sodium nitrate</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
</tr>
<tr>
<td>CuSO₄·5H₂O</td>
</tr>
</tbody>
</table>

Water to make 1000 cc.

pH, approx. 5–5.3.

Operating temperature, 150° F.

A wetting agent, such as the dibenzyl ester of sodium sulfosuccinic acid may also be added to increase the uniformity of the deposit.

The above bath was used with a nickel-copper alloy (Ni 30%) and deposits, which are denoted in Table I, were produced according to the following current densities and bath agitation:

<table>
<thead>
<tr>
<th>Ampères per sq. ft.</th>
<th>Still</th>
<th>Slow</th>
<th>Medium</th>
<th>Fast</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.</td>
<td>Semi-bright, Ni-color.</td>
<td>One streak (matte) increasing in amount toward top of panel.</td>
<td>Irregular dark brick, gray, and Ni-color, matte.</td>
<td></td>
</tr>
</tbody>
</table>

A determination of the resistance of sample panels to corrosion was made by the Corrodke test, and by outdoor exposure. The Corrodke test is carried out by preparing a special paste, brushing the paste on each of the test panels and maintaining the paste coated panels in a humidity test cabinet which is so operated as to provide a non-condensing atmosphere. The special paste is prepared by: measuring out 7.0 ml. of a cupric nitrate solution (2.50 grams of cupric nitrate in 500 ml. of water) and placing it in a 250 ml. glass beaker, measuring out 33 ml. of ferric chloride solution (2.50 grams of ferric chloride in 500 ml. of water) and placing it in the beaker with the 7 ml. of cupric nitrate, measuring out 10.0 ml. of ammonium chloride solution (50.0 grams of ammonium chloride in 500 ml. of water) and placing it in the beaker with the 7 ml. of cupric nitrate and 33 ml. of ferric chloride, weighing out 30 grams of kaolin and adding it to the reagents in the beaker and mixing all the ingredients until a homogeneous slurry or paste is obtained.

Four sample panels were prepared as follows for purposes of corrosion determination:

1. Copper strike + 0.5 mil bright copper + 0.5 mil bright Ni-Cr
2. Copper strike + 0.5 mil copper-nickel (30% Ni) + 0.5 mil bright Ni-Cr
3. Copper strike + 1.2 mil copper-nickel (30% Ni) + Cr
4. Copper strike + 1.0 mil bright Ni-Cr

After a 20 hour corrosion test by the Corrodke method, the deposits showed the following defects:

Sample No. 1—Excessive rust stain and pin-point holes to the steel.
Sample No. 2—Perfect panel, no rust whatsoever.
Sample No. 3—Good panel despite the fact that the edges were buffed thinner than 1 mil and the panel showed numerous pits along both edges after buffing. These pits, after Corrodke, appeared to contain very little rust. Some edge rust corresponded to areas buffed most.
Sample No. 4—Moderate amount of rust stain and pin-point holes.

It should be understood that copper-nickel alloy anodes, other than 30% nickel anodes, will yield improved corrosion resistance and are contemplated by the invention. Any copper-nickel alloy anode having from 30% to 75% nickel is suitable. The copper-nickel alloy undercoat deposit may be from 30% to 75% nickel; 50% being preferred.

Replicate panels exposed in a semi-industrial atmosphere for nine months showed the same trend as obtained in Corrodke test. Since the Corrodke test does not always give the same results as atmospheric tests, this comparison shows that for these systems the Corrodke test is satisfactory.

In another test 6" x 1½" steel panels were bent prior to plating, so that a recessed area existed. These were plated similarly to those above, using a nickel strike instead of a copper strike but omitting No. 3. The average thickness was the same as above but, of course, the deposit thickness on the projecting areas were higher and on the recessed areas lower than the uniform thicknesses given above. These were Corrodke tested. There was practically no corrosion on the projecting areas of any of the panels, where the deposit thickness was heavy. The results in the recessed areas were as follows:

1. (1) Excessive rust;
2. (2) Slight rust;
3. (3) Excessive rust; worse than No. 1.

It will be understood that the aluminum would be given any of the preliminary treatments necessary to effect good adhesion of the copper or nickel to the aluminum. The best known of these are the zincate treatment which first applies a very thin coating of zinc on the surface, and the anodizing method which first applies a porous oxide coating on the aluminum surface.

Having thus disclosed my invention, what I claim is:

1. A process for the electrolytic preparation of a corrosion resistant article comprising electrodeposition on a basis metal selected from the class consisting of aluminum, iron and zinc and alloys thereof, a metal undercoat selected from the class consisting of copper and nickel, electrodeposition a copper-nickel alloy on said metal undercoat and electrodeposition a nickel coating on said copper-nickel alloy, said electrodeposited materials being free of heat treating.
2. A process for the electrolytic preparation of a corrosion resistant article comprising electrodeposition on a basis metal selected from the class consisting of aluminum, iron, and zinc and alloys thereof, a metal undercoat selected from the class consisting of copper and nickel, electrodeposition a copper-nickel alloy on said metal undercoat, electrodeposition a nickel coating on said copper-nickel alloy and electrodeposition a chromium layer on said nickel coating, said electrodeposited materials being free of heat treating.
3. A process for the electrolytic preparation of a corrosion resistant article comprising electrodeposition on a basis metal selected from the class consisting of aluminum, iron, and zinc and alloys thereof, a metal undercoat 0.05 to 0.3 mil thick selected from the class consist-
3,247,082

ing of copper and nickel, electrodepositing a copper-nickel alloy 0.3 to 1.0 mil thick on said metal undercoat, electrodepositing a bright nickel coating 0.2 to 1.0 mil thick on said copper-nickel alloy and electrodepositing a chromium layer 0.005 to 0.1 mil thick on said nickel coating, said copper-nickel alloy being free from heat treating and being electrodeposited from an aqueous plating solution comprising copper sulfate, nickel sulfate and sodium citrate having a copper-nickel alloy containing approximately 30% nickel anode disposed therein, whereby improved thickness distribution of said copper-nickel alloy is obtained.

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