ABSTRACT OF THE DISCLOSURE

A preplating treatment for nickel plating onto zinc in which the zinc is first coated with a film of an alkyl or an alkanoamine prior to immersion into the nickel plating bath.

This invention relates generally to the nickel plating of zinc and, more specifically, to a preplating treatment for use prior to the actual plating sequence. The pre-plating treatment of our invention is most significantly effective when used prior to practicing the nickel plating process disclosed and claimed in copending U.S. patent application Ser. No. 516,761, Baig, filed Dec. 27, 1965 now U.S. Pat. No. 3,417,005. However, the process disclosed and claimed herein is applicable to other nickel plating processes too. The previously mentioned Baig patent application is directed toward a nickel electrodeposition bath and the process for its use. The bath disclosed and claimed therein, briefly described, comprises:

At 0.53 mole/liter of nickel ion (Ni^{++}); at least 0.45 but less than 0.54 mole/liter of citrate ion (C_6H_5O_7^{-};); at least 0.023 mole/liter of gluconate ion (C_6H_5O_7^{-};); in the group consisting of Cl^{-} and F^{-} for inducing anode corrosion; and, as an additive, from the group consisting of (NH_4)^{+} and (triethanolamine) for relieving stresses in the deposit.

More specifically, the Baig bath comprises:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Grams per liter</th>
<th>Moles per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (Ni^{++})</td>
<td>21-2</td>
<td>0.30-0.6</td>
</tr>
<tr>
<td>Citrate (C_6H_5O_7^{-};)</td>
<td>80-100</td>
<td>0.65-0.84</td>
</tr>
<tr>
<td>Gluconate (C_6H_5O_7^{-};)</td>
<td>0.6-0.40</td>
<td>0.05-0.30</td>
</tr>
<tr>
<td>Chloride (Cl^{-})</td>
<td>1-2</td>
<td>0.008-0.06</td>
</tr>
<tr>
<td>Ammonium (NH_4)^{+}</td>
<td>1-2</td>
<td>0.050-0.30</td>
</tr>
</tbody>
</table>

Briefly stated, our invention comprises immersing a nickel article into a nickel complexing film-forming alkyl or alkanoamine immediately prior to the immersion of the article into the nickel plating bath. By nickel complexing film-forming alkyl or alkanoamine, we mean to include such compounds as the methyl, ethyl, and propyl amines, the methanol, ethanol, and propanol amines, and the ethylene and propylene diamines and derivatives thereof, such as ethylene diamine tetraacetic acid. Aqueous solutions of triethanolamine have been found to be significantly effective. In our preferred process for nickel plating zinc base die castings, we immerse them for 15-30 seconds in a 2-10% by volume solution of triethanolamine and then electroplate them with the bath disclosed as preferred for zinc base die castings in the aforementioned Baig patent application. This preferred Baig bath as disclosed in the aforementioned copending application comprises:

<table>
<thead>
<tr>
<th>Salt</th>
<th>Grams per liter</th>
<th>Moles per liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO_4.6H_2O</td>
<td>140-280</td>
<td>0.50-1.00</td>
</tr>
<tr>
<td>Na_2C_2O_4.2H_2O</td>
<td>120-145</td>
<td>0.45-0.83</td>
</tr>
<tr>
<td>Na_2CO_3</td>
<td>19-20</td>
<td>0.46-0.14</td>
</tr>
<tr>
<td>CF_3</td>
<td>8-12</td>
<td>0.25-0.54</td>
</tr>
<tr>
<td>NaF</td>
<td>8-13</td>
<td>0.64-0.18</td>
</tr>
</tbody>
</table>

Note—pH 7.5-7.7, Temperature 180-190°F.

Any nickel salt can be used as a source of nickel ions, such as nickel chloride, nickel fluoroborate, nickel sulfonate, or nickel acetate. However, the best results have been obtained using nickel sulfate, commercially available in the 6-hydrate or 7-hydrate forms.

Concentrations of less than 2% by volume of triethanolamine improve the adhesion of nickel to zinc, which has been treated therewith. However, the improvement in adhesion does not become significant until concentrations in excess of 2% are employed. Concentrations in excess of 10% are effective, but not necessary, and in some respects may even be undesirable, as will be discussed hereinafter in conjunction with the undesirable effects incident to drag-out from the pretreatment bath.

The following is a preferred process that is intended merely to serve as a specific example of our invention for producing an improved, more strongly adherent electrodeposited nickel coating on zinc. An unbuffed zinc die casting such as a door handle was cleaned anodically at a current density of about 50 a.s.f. by immersion into a commercial alakline cleaner, such as Northwest #371, and was treated therewith for about one minute at about 150°F. The part was subsequently rinsed in water followed by a 10 second dip at room temperature in a 4 oz./gal. aqueous solution of an acid salt, such as Northwest Actisalt #1, and a wetting agent, such as Northwest Addition Agent #9. The acid dip was followed by a water rinse. The part was next dipped for about 30 seconds in a 100 ml./gal. (2.5% by volume) aqueous solution of triethanolamine at room temperature. Immediately, without rinsing, the thus treated part was immersed live into a bath comprising:

<table>
<thead>
<tr>
<th>Salt</th>
<th>G./l.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate</td>
<td>142.2</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>29.92</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>140</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>29.92</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>33.9</td>
</tr>
</tbody>
</table>

The bath had a pH of 7.0 and was maintained at a temperature of about 140°F. Live entry at a strike current density of 150 a.s.f. for about 30 seconds followed by a normal plating current density of 40 a.s.f. for 14 minutes produced optimum coverage and adhesion. A dual chrome layer was then applied in the normal and accepted manner. However, the post nickel plating steps chosen are

This and other objects of our invention will become apparent from the detailed description which follows.
wholly dependent upon the nature of the article sought
3 to be produced and may comprise any of the conventional
4 plating sequences known in the art.

5 We prefer to use the lowest concentration of amine
6 which will produce the desired nickel complexing film.
7 This is preferred in order to prevent any substantial drag-
8 out and incident build-up of amine in the nickel plating
9 bath. Hence, for example, the Baig bath has a limited
10 tolerance for triethanolamine as disclosed in the afore-
11 mentioned application. Too high a triethanolamine con-
12 centration in the bath tends to produce a cracked deposit.
13 Hence, by reducing the concentration of the amine, e.g.,
14 triethanolamine, in the preplating treatment step, con-
15 tinuous plating may be effected for a longer period of
16 time before the nickel plating bath must be decontami-
17 nated or replaced. As the plating baths vary, so also will
18 their respective tolerances for amines. Hence, the par-
19 ticular plating bath selected from the many known in
20 the art will, in many respects, dictate not only the par-
21 ticular choice of amines, but also the optimum concen-
22 tration for its use with that particular bath.

23 The treatment of our invention forms a film over the
24 surface of the article. Exactly what function this film
25 performs is not known. One possible explanation is that
26 the film insulates the surface from oxidation during its
27 traverse from the pretreatment tank to the plating tank
28 and that the film is destroyed upon entry into the plating
29 tank. Another possible explanation may reside in the fact
30 that only compounds which are known to complex nickel
31 seem to be effective and that it is the ability to complex
32 that produces the improved result. We do not intend, how-
33 ever, to be bound by either of these theories.

34 While we have disclosed our invention in conjunction
35 with a specific embodiment, we do not intend to limit
36 ourselves, except as by recited in the claims appended
37 hereto.

38 We claim:

39 1. A process for nickel plating zinc articles comprising
40 the successive steps of immersing a zinc article into a
41 nickel complexing agent consisting essentially of an aque-
42 ous solution containing at least about 2% of a compound
43 selected from the group consisting of alkylamines and
44 alkanol-aminos, and thereby forming a film of said nickel
45 complexing agent on the surface of said zinc article; im-
46 mediately subsequently immersing said zinc article already
47 coated with said film of nickel complexing agent into a
48 nickel salt solution; and electrodepositing a strongly ad-
49 herent nickel coating from the nickel salt solution onto
50 the surface of the zinc article.

51 2. A process as described in claim 1 wherein said
52 selected compound is triethanolamine.

53 3. A process as described in claim 2 wherein said nickel
54 salt solution has a pH of about 5.0–9.5 and comprises:
55 (a) a nickel ion concentration of at least 0.53 mole/liter
56 produced from salts selected from the group consisting of
57 nickel sulfate, nickel chloride, nickel fluoride, nickel
58 sulfonate, and nickel acetate, (b) a citrate ion concentra-
59 tion of at least 0.45 but less than 0.54 mole/liter of
60 solution, (c) a gluconate ion concentration of at least
61 about 0.023 mole/liter of solution, (d) an ion for induc-
62 ing anode corrosion selected from the group consisting of
63 chloride and fluoride, and (e) an additive for reducing
64 stress in the deposit selected from the group consisting
65 of ammonium ions and triethanolamine.

66 4. The process as claimed in claim 1 wherein the con-
67 centration of said nickel complexing compound is about
68 2–10% by volume, the balance being water.

69 5. The process as claimed in claim 4 wherein said com-
70 plexing compound is triethanolamine.

71 6. The process as claimed in claim 5 wherein the nickel
72 salt solution has a pH of about 5.0–9.5 and comprises:
73 (a) a nickel ion concentration of at least 0.53 mole/liter
74 produced from salts selected from the group consisting
75 of nickel sulfate, nickel chloride, nickel fluoride, nickel
76 sulfonate and nickel acetate, (b) a citrate ion concentra-
77 tion of at least 0.45, but less than 0.54 mole/liter of
78 solution, (c) a gluconate ion concentration of at least
79 about 0.023 mole/liter of solution, (d) at least one ion
80 for inducing anode corrosion selected from the group con-
81 sisting of chloride and fluoride, and (e) an additive for
82 reducing stress on the deposit selected from the group
83 consisting of ammonium ions and triethanolamine.

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