United States Patent Office

3,041,254

Patented June 26, 1962

NICKEL PLATING


No Drawing. Filed Jan 25, 1960, Ser. No. 4,176
Claims priority of application in Great Britain Jan. 30, 1959, 2 Claims. (Cl. 204—49)

This invention relates to the direct nickel plating of metallic objects, more especially of zinc alloy die-castings.

The established practice for nickel plating zinc alloy die-castings involves the deposition of a primary copper coating directly upon the zinc alloy, nickel being subsequently plated upon the copper. It is thought that this copper coating has little protective value, and it may be difficult to remove the powder since diffusion of copper into the zinc alloy is possible, and this would adversely affect the quality of the die-cast product. Any fault in the copper layer may cause subsequent blistering of the nickel plate and failure of the plated zinc alloy die-casting. It is therefore an object of this invention to plate zinc-alloy directly with nickel without an intermediate copper layer.

Some slight success in this direction has previously been attained with the use of plating solutions of nickel sulphate at a pH of about 6. Under these acid conditions zinc tends to go into the solution, either by acid attack, or by the formation of displacement coatings of nickel, in each case the effect on the final electro-deposit is very detrimental. The tendency for zinc to dissolve is accentuated at cavities in the casting (when the throwing power of the solution is poor), while in solutions with a reasonable throwing power, burning has occurred at points where the current density is high. All this has meant that only castings of comparatively simple design could be directly nickel plated under acid conditions.

It is known from U.S. Patent No. 2,069,566 that zinc may be directly plated with nickel under alkaline conditions. The nickel solution is used, together with additions of acid citric, sodium pyrophosphate, sodium bisulphite, sodium citrate and sodium chloride. The pH is maintained at 7.5–9.0 with ammonia. This bath appears to have good throwing power, and to be free from burning, with a better toleration for zinc than plating solutions of lower pH values. However, the presence of much sodium in the solution is believed to cause stresses in the deposit. The citric acid included in the solution would be expected to precipitate, as zinc citrate, any zinc which went into solution. However, this does not occur in the presence of ammonia, and the quality of the plate would be adversely affected by the zinc remaining in solution.

The present invention consists in the method of depositing nickel directly on to zinc alloy die-castings from alkaline solutions of nickel citrate. In such solutions, nickel citrate acts as both the source of nickel and as the complexing agent necessary to maintain solubility in alkaline solution.

Although a good dull deposit may be obtained from an alkaline solution of nickel citrate alone, other agents may be present in the solution to improve the quality of the deposit. For example a chloride may be added to improve anode corrosion, nickel citrate to help maintain solubility and nickel formate to improve the quality of the deposit.

If brighter deposits are desired formaldehyde and saccharin may be added as brightening agents.

Alternatively, the original dull deposit of nickel may be used as a basis for a bright nickel deposit from a conventional acid bath. Thus, the invention further con-
Zinc alloy die-castings were plated in a bath containing:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Gms./litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>169</td>
</tr>
<tr>
<td>Nickel (as carbonate)</td>
<td>71.2</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>36.2</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>20</td>
</tr>
<tr>
<td>Nickel formate</td>
<td>15</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>37.2</td>
</tr>
</tbody>
</table>

The pH was maintained at above 7.7, the current density was 30 amps./ft.² and the temperature was 60° C. The same final composition, i.e. the preferred composition may be obtained by using the following reagents:

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Gms./litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric acid</td>
<td>195</td>
</tr>
<tr>
<td>Nickel (as carbonate)</td>
<td>71.2</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>20</td>
</tr>
<tr>
<td>Nickel formate</td>
<td>15</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>52</td>
</tr>
</tbody>
</table>

In this case additional NaOH is required to neutralise the excess citric acid added to form sodium citrate. Using this solution a good deposit is obtained, suitable as a primary deposit in place of the usual copper layer over which a further thickness of nickel is deposited from a conventional acid nickel bath. This alkaline citrate solution has a much better throwing power than a conventional acid nickel bath, thus making it very suitable for the initial deposit on a zinc alloy die-casting.

Example III

A polished zinc alloy die-casting was plated at 30 amps./ft.² to a thickness of 0.3 to 0.4 mil in the solution of Example II. The sheet was then overplated in a commercial acid "bright" nickel bath at 60 amps./ft.² to a total nickel thickness of 1.0 to 1.1 mil. The final appearance was fully bright and shining.

Example IV

The addition of 3 to 4 mil/litre of 40% formaldehyde solution and 0.2 to 1.0 gm./litre of saccharin to the solution of Example II results in a fully bright deposit.

References Cited in the file of this patent

UNITED STATES PATENTS

1,991,747 Hogaboom Feb. 19, 1935
2,069,566 Tuttle Feb. 2, 1937
2,356,368 Pray Dec. 14, 1944
2,359,158 Moy Jan. 30, 1951
2,782,152 Durose et al. Feb. 19, 1957
2,879,211 Kardos et al. Mar. 24, 1959

We have been able to use current densities of from 20 to 70 amps./ft.² which are higher values than those said to be possible in U.S. Patent 2,069,566.

It is worthy of note that the addition of ammonia to the solution preferred for plating with a dull deposit raises the pH to 9.5 to 10.5. This results in an improved current density range of from 20 to 50 amps./ft.² and an efficiency of 100%. The deposit produced is semi-bright and suitable for overplating with a conventional acid nickel plate.

It is to be understood that while this invention particularly relates to nickel plating directly on to zinc-alloy die castings, it may also apply to nickel plating on steel or brass objects.

Various modifications may be made within the scope of the invention.

1. In a solution for electrolytically depositing nickel, the improvement comprising 120 to 175 mg./l. of citric acid, nickel carbonate to saturation, 10 to 20 gm./l. of nickel chloride hexahydrate, 15 to 25 gm./l. of sodium citrate with a pH value maintained at 7.0 to 7.5 with sodium hydroxide, 10 to 40 gm./l. of nickel formate, 2 to 5 gm./l. of formaldehyde and 0.2 to 1.0 gm./l. of saccharin.

2. In a solution for electrolytically depositing nickel, the improvement comprising 120 to 175 gm./l. of citric acid, 64 to 78 gm./l. of nickel carbonate, 36 to 47 gm./l. of sodium citrate, 20 to 25 gm./l. of nickel chloride, 34 to 43 gm./l. of sodium hydroxide 10 to 40 gm./l. of nickel formate, 2 to 5 gm./l. of formaldehyde and 0.2 to 1.0 gm./l. of saccharin.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,041,254
June 26, 1962

Alan Edward Pedler

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 40, for "plate" read -- plated --;
column 4, line 21, for "mg./l." read -- gm./l. --;
line 28, for "120 to 175" read -- 152 to 186 --.

Signed and sealed this 23rd day of October 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents