

1

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ALKALINE NICKEL PLATING SOLUTION

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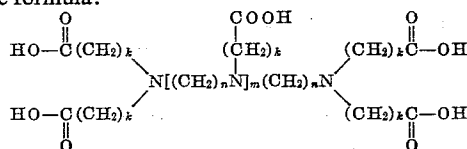
5 Claims. (Cl. 204—49)

This invention relates to electrodeposition of nickel and more specifically to alkaline nickel plating solutions and processes of electrodeposition utilizing such solutions.

Several alkaline nickel plating solutions have been devised in the past but, so far as we are aware, they have left much to be desired either in the quality of the deposit or in the behavior of the solution.

We have now discovered that by the inclusion in the alkaline nickel solution of one or more compounds of a class of complexing agents not to our knowledge heretofore employed in such solutions, we are able to produce consistently excellent deposits on zinc base die castings and other bodies composed or largely composed of zinc and that such solutions exhibit very much improved stability. The complexing agents referred to are the polyalkanoic acid derivatives of polyalkylene amines.

The compounds of this class which we prefer to use are of the formula:



where n is an integer from 2 to 3, m is an integer from 0 to 2 and k is an integer from 1 to 4.

In the practice of the invention, nickel is supplied by maintaining in the plating solution a suitable source of nickel which desirably may be nickel sulfate, nickel chloride or a mixture thereof. While good deposits can be produced from an aqueous solution containing only the nickel compound and the complexing agent (e. g. at two parts nickel sulfate hexahydrate and one part ethylene diamine tetra acetic acid to twenty parts water, all by weight), it is desirable to have present in the solution other agents which serve useful purposes. In order to maintain conveniently an optimum pH range a buffering agent should be included. This may be for example sodium citrate. We have found also that an organic amine such as an alkanolamine having from 3 to 12 carbon atoms in the molecule (e. g. triethanolamine) has a definite stabilizing influence on the nickel complex, maintaining solubility under conditions which would otherwise result in precipitation. The chloride radical increases anode corrosion while the nitrate radical decreases hydrogen evolution and permits higher current densities. Ammonium salts, e. g. NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$, although not indispensable, somewhat improve lustre, ductility and cathode efficiency. They may be present in proportion from 5 to 35 grams per liter.

Representative specific polyalkanoic acid derivatives of polyalkyleneamines suitable for realization of the invention are as follows:

- (1) Ethylene diamine tetra acetic acid.
- (2) Diethylene triamine penta acetic acid.
- (3) Mono sodium salt of ethylene diamine tetra acetic acid.

2

- (4) Disodium salt of ethylene diamine tetra acetic acid.
- (5) Trisodium salt of ethylene diamine tetra acetic acid.
- (6) Tetra sodium salt of ethylene diamine tetra acetic acid.

- 5 (7) Monosodium salt of diethylene triamine penta acetic acid.

- (8) Disodium salt of diethylene triamine penta acetic acid.

- 10 (9) Trisodium salt of diethylene triamine penta acetic acid.

- (10) Trisodium salt of triethylene tetramine hexa acetic acid.

- (11) Propylene diamine tetra acetic acid.

- 15 (12) Trisodium salt of propylene diamine tetra acetic acid.

- (13) Trisodium salt of propylene diamine tetra propionic acid.

- (14) Trisodium salt of dipropylene triamine penta propionic acid.

Solutions according to the invention should be operated at a pH in the range from 6.5 to 12, most suitably from pH 7.0 to pH 8.0. Cathode current density may be from 30 to 80 amperes per square foot. Temperature may be from normal room temperature to 160° F., most suitably from 120° F. to 140° F.

Concentrations per liter of the various agents present in which the solutions in addition to water may be as follows: Nickel compound supplying nickel ions, molecular equivalent of from 75 to 350 grams of nickel sulfate hexahydrate; complexing agent from 25 to 175 grams; stabilizing agent, optional from 25 to 200 grams; and nitrate ion, optional, from 5.0 to 40.0 grams. Preferred solutions are as follows:

35 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 75 to 350, preferably 85 to 210 g./l.

Ethylene diamine tetra acetic acid, 25 to 175, preferably 25 to 150 g./l.

Triethanolamine, 0 to 200 cc., preferably 25 cc. to 100 cc./l.

40 Nickel nitrate, 0 to 40 preferably 5.0 to 30 g./l.

NaCl , 0 to 200, preferably 25 to 150 g./l.

pH, 6.5 to 12, preferably 6.8 to 9.0

C. D. (amperes per sq. ft.), 10 to 150, preferably 20 to 80
Temperature (degrees F.), 100 to 180, preferably 120 to 140

The following specific examples of the practice of the invention, incorporating the various ingredients which have been found beneficial will serve as illustrations:

Example I

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	100 g./l.
Na citrate.....	66 g./l.
NaCl or NH_4Cl	35 g./l.
Ethylene diamine tetra acetic acid	20-100 g./l. (e. g., 60).
Triethanolamine	35-50 cc. (e. g., 40).
$\text{Ni}(\text{NO}_3)_2$	10-30 g./l. (e. g., 20).
pH	6.5-12 (e. g., 7.0).
Current density.....	40 amp./ft. ² .
Temp.....	140° F.
NaHSO_3	3-8 g./l. (e. g., 5).

Example II

NaHSO_3	g./l.	3-8
NiCl_2	g./l.	85
Na citrate	g./l.	66
Na_2SO_4	g./l.	75
Ethylene diamine tetra acetic acid.....	g./l.	40
Triethanolamine	cc.	40
$\text{Ni}(\text{NO}_3)_2$	g./l.	20
pH (with NaOH).....		7.5

Current density-----amp./ft.² 40
Temp. -----°F 140

Results of plating tests with these two baths at 140° F. were very satisfactory. In all cases the deposits were dull semi-bright with fine grained and dense deposits resembling those deposits which are obtained from the Watts bath and all deposits were ductile with excellent adhesion. Furthermore, stability of these solutions is excellent.

Example III

NiSO₄·6H₂O -----g./l. 100
Ethylene diamine tetra acetic acid-----g./l. 65
pH ----- 6.8-10

Example IV

NiCl₂ -----g./l. 85
Ethylene diamine tetra acetic acid-----g./l. 65
pH ----- 6.8-10

These two solutions give good deposits and exhibit excellent stability. The deposits are not, however lustrous as in the case of Example I and II.

Having thus described the invention, what we now claim is:

1. An aqueous, alkaline nickel plating solution comprising a nickel compound of the class consisting of nickel chloride, nickel sulfate and mixtures thereof molecularly equivalent to 75 to 250 grams per liter of nickel sulfate hexahydrate, a complexing agent in concentration from 25 to 175 grams per liter, said complexing agent being a polyalkanoic acid derivative of a polyalkylene amine soluble in the solution, and a polyalkanol amine stabilizer present in concentration from 25 to 200 grams per liter, the pH of said solution being in the range from 6.5 to 12.

2. An electroplating process comprising passing current from a nickel anode to a cathode to be coated through an aqueous, alkaline nickel plating solution comprising a nickel compound of the class consisting of nickel chloride, nickel sulfate and mixtures thereof molecularly equivalent to 75 to 250 grams per liter of nickel sulfate hexahydrate, a complexing agent in concentration from 25 to 175 grams per liter, said complexing agent being a polyalkanoic acid derivative of a polyalkylene amine soluble in the solution, and a polyalkanol amine stabilizer present in concentration from 25 to 200 grams per liter,

the pH of said solution being maintained in the range from 6.5 to 12, the temperature being maintained in the range from 100° F. to 180° F. and the current density being maintained in the range from 20 to 80 amperes per square foot.

3. An aqueous, alkaline nickel plating solution comprising, in addition to water, from 85 to 210 grams per liter of nickel sulfate hexahydrate, from 25 to 150 grams per liter of ethylene diamine tetra acetic acid, from 25 to 100 grams per liter of triethanolamine, the pH of said solution being from 6.8 to 9.0.

4. An electroplating process comprising passing current from a nickel anode to a cathode to be coated through an aqueous alkaline nickel plating solution comprising, in addition to water, from 85 to 210 grams per liter of nickel sulfate hexahydrate, from 25 to 150 grams per liter of ethylene diamine tetra acetic acid and from 25 to 100 grams per liter of triethanolamine, the pH being maintained in the range from 6.8 to 9.0, the temperature being maintained in the range from 120° F. to 140° F. and the cathode current density being maintained in the range from 20 to 80 amperes per square foot.

5. An aqueous, alkaline nickel plating solution comprising nickel sulfate equivalent to 75 to 250 grams per liter of nickel sulfate hexahydrate, a complexing agent in concentration from 25 to 175 grams per liter, said complexing agent being a polyalkanoic acid derivative of a polyalkylene amine soluble in the solution, a polyalkanol amine stabilizer in concentration from 25 to 200 grams per liter, a buffering agent and from 5 to 30 grams per liter of nickel nitrate, the pH of said solution being in the range from 6.5 to 12.

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