Nickel Coatings With Special Properties

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A solution and process for electroplating of Ni coatings with special properties was developed. Coatings have these advantages: high plating rates (two to three times higher than from agitated Watt's solution); parts may be connected to an external electric circuit by point-welding, using conductive glue or by soldering with inactive fluxes; and high adhesion to thermoplastic resins. To make a contact between a component and an external circuit, no additional second local coating is required. It is possible to carry out local (selective) plating even after storage of nickel-plated parts (as long as for 10 days) without any additional pretreatment. Nickel coating can be applied as an underlayer for gold and silver plating for electronic components, such as a substrate for intergrated circuits, contactors and switches, treated in Reel-to-Reel lines. Any corrosion in the pores of a local coating (if there are such pores) is excluded. Also, there is no transfer of corrosion products of an underlayer onto the contacting surface (the local coating). Because of the combination of high ductility and sufficient hardness, Ni coating can withstand deformation (bending, compession, etc.).

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Introduction

Nickel plating has many applications in industry. Watts'-type bath is most widely used and it contains high concentration of nickel ions – from 60 to 150 g/l¹. This bath is characterized by high nickel ions drag-out. Therefore one of promising ways to improve environmental characteristics of nickel plating process is the implementation of nickel plating baths with low concentration of nickel salts, which, on the other hand, can insure high deposition rate and required characteristics of the coatings.

Results and Discussion

In the present work a new formulation of nickel plating bath has been developed which provides high deposition rate at lover concentrations of nickel ions – 6 to 30 g/l. The bath is based on a combination of nickel chloride and nickel acetate. Results of the experiments have shown that light-grey nickel coatings can be obtained at nickel content 6 g/l (bath No1), pH of 4.5, 50°C over C.D. range 1 to 6 A/dm² with C.E. 86.5-87.5%. This corresponds to nickel deposition rate from Watts'-type solution with nickel content 60-120 g/l.

At higher nickel concentration in acetate-chloride solution - up to 18 g/l (bath No2) C.D. range expands to 1-10 A/dm² and C.E. becomes also a little higher – 87-91%. At still higher nickel content – 30 g/l (bath No3) upper limit of cathode C.D. becomes as high as 22 A/dm². and C.E. – 89-93% (Fig.1).



Fig. 1. C.E. vs. C.D. Curves number corresponds to solutions number; t 50 °C, pH 4,5.

Operation at lower pH allows to increase cathode C.D. still further: e.g. at pH=4.0 in bath No1 – up to 15 A/dm², and in bath No3 up to 60 A/dm². Of course, C.E. becomes slightly lower: 62-64% in bath No1, 69-84% - in bath No3.

Potentiometric titration with sodium hydroxide of all above solutions has revealed that maximum buffering ability of acetate-chloride solutions corresponds to pH range 4.0-5.5, which is close to pK of acetic acid². Buffering ability becomes lower in solutions with lower concentrations of nickel salts. However, even at minimum concentrations of nickel ions (6 g/l) buffering ability is 16-52 times of that in Watts'-type solutions. Formation of nickel hydroxide in acetate-chloride solutions takes place at higher pH values (7.75, bath No1; 7.42, bath No2; 7.32 bath No3) than in Watts'-type bath (5.8-6.0). These principal differences in the behavior of nickel ions in conventional and new solutions are related with the formation of nickel complexes in acetate-chloride solutions, such as $[Ni(CH_3COO)]^+$, $[NiCl]^+$, $[Ni(CH_3COO)_2]^0$, $[NiCl_2]^0$. Formation of complexes shifts pH of hydroxide formation upwards.

Since acetic acid is contained practically in a molecular form and new plating solutions contain no salts other than nickel ones these solutions should be considered as free of foreign electrolytes.

There is a principal difference between the electrode reactions taking place in Watts'-type and acetate-chloride solutions³. Ni²⁺ cations and hydroxonium cations are discharged in Watts'-type solutions:

$Ni^{2+}+2e \rightarrow Ni^{0}$	(1)
$2H_3O^++2e \rightarrow H_2+2H_2O$	(2)

Reaction (2) creates a deficit of hydrogen ions and is responsible for the hydrolysis of nickel salts. A discharge of nickel complexes at the cathode in acetate-chloride solutions is releasing free acetate and chloride ions:

$$NiAc_{1 \text{ or } 2}, NiCl_{1 \text{ or } 2}+2e \rightarrow Ni+(1 \text{ or } 2) \text{ Ac}^{-}, (1 \text{ or } 2) \text{ Cl}^{-}$$
(3)

which act as buffering agents, preventing pH increase caused by the reaction (2).

Apart from that the formation of these two anionic species requires the presence in the vicinity of the metal/solution interface of the equivalent amounts of cations. Hydroxonium and few types of nickel-containing ions are only available types of cations. Therefore, they are forced by additional potential gradient to arrive into the cathode layer in order to fulfill the electric neutrality principle, both in the bulk solution and inside the cathode layer. Additional potential gradient facilitates also the mass transport of both hydroxonium and nickel-containing cations across the cathode diffusion layer (so called "exhaltaion" of the migration component of the total current density). Therefore, effective prevention of nickel salts hydrolysis, which is major cause of limitations of nickel deposition rate, is accomplished by simultaneous mechanisms: more efficient transport to the cathode of metal–and hydrogen-containing ions and reducing the activity of Ni²⁺ ions due to the formation of complexes and the shift in the corresponding equilibrium created by the release of ligands according to the reaction (3).

Acetate-chloride baths have high throwing power (TP), which is increasing, if the concentration of nickel ions is decreased from 30 g/l (TP=15.7% at 5 A/dm² and 17.8% at 2

 A/dm^2) down to 6 g/l (TP=26.7% at 5 A/dm² and 30.3% at 2 A/dm²). An increase in the cathode current density causes, as usually, a decrease in the throwing power (Fig.2).



Fig.2. Throwing power respect to metal vs. C.D. Curves number corresponds to solutions number; t 50 °C, pH 4,5.

Nickel coatings obtained have better mechanical characteristics: higher hardness (2,5 to 3,2 GPa), which does not show strong dependence on the concentration of nickel salts or solution pH (Fig.3). Coatings obtained at low current densities (1-2 A/dm²) are harder than those obtained at higher C.D., probably due to greater hydrogen inclusion. Slight increase in the hardness observed at pH 4.5 near the upper limit of cathode current density is obviously related with the inclusion of nickel hydroxide.



Fig.3. Hardness of Ni-coatings vs. C.D. Curves number corresponds to solutions number; t 50 °C, pH 4,5.

Nickel coatings obtained from low concentration solution (6-18 g/l Ni) have low tensile stress of 16-32 MPa (Fig.4, curves 1&2). Most ductile deposits were obtained from the bath No 1 at 2-5 A/dm² and No 2 at 5-10 A/dm². The ductility of deposits is much higher than that of the deposits obtained from Watts'-type bath and is close to that of copper coatings.

Electrical specific resistance for the coatings obtained at 2 A/dm^2 is close to that of metallurgical nickel – 7.1 to 7.7*10⁻⁸ Ohm*m (Fig.5). Such values are an indication of high purity of deposits. Porosity of the coatings becomes lower at lower concentration of nickel salts and, as usually, is reducing with increasing plate thickness. At 9 to 12 µm the coatings become practically poroless. Such exceptionally low porosity of Ni coatings is probably related with high purity of deposits and low stresses. Any corrosion in the pores of a local coating (if there are such pores) is excluded. Also there is no transfer of corrosion products of an underlayer onto the contacting surface (the local coating).



Fig.4. Internal stress of Ni coatings (20 **m** thick) vs. C.D. Curves number corresponds to solutions number; t 50 °C, pH 4,5.



Fig.5. Specific resistance (**r**) *of Ni deposits* (20 **m***n vs. C.D. Curves number corresponds to solutions number; t 50°C, pH 4,5.*

The coatings obtained in acetate-chloride solutions have been tested in an industrial plant producing electronic components and devices. Results of the tests have shown that coatings have these advantages: parts may be connected to an external electric circuit by point-welding or using conductive glue or by soldering with inactive fluxes. To make a contact between a component and an external circuit no additional second local coating is required. It is possible to carry out local (selective) plating even after storage of nickel-plated parts (as long as for 10 days) without any additional pretreatment, which is usually necessary before next plating stage. Nickel coating can be applied as an underlayer for gold and silver plating for electronic components, such as a substrate for integrated circuits, contactors and switches, etc.

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