Electroless nickel plating in solutions containing acetate, lactate, citrate and glycine as ligands has been studied at pH 4.5 and a temperature of 85 °C. A decrease in nickel plating rate and an increase in P amount incorporated into the coatings have been found to be proportional to the increase in stability of Ni^{2+} ions complexes with organic acid ions and are related to their steric and adsorption hindrance on the nickel surface. This is distinctly expressed at higher concentrations of glycine and citrate bound with nickel in a more complicated manner, if compared to acetate and lactate.

0.2 mM CuSO_4 stabilize all the electroless plating solutions studied and increase the nickel plating rate. The Cu content in the coatings varies in the range 0.8 to 1.3 wt.%. The presence of dicarboxylic acid (malonic, succinic or adipic) along with Cu^{2+} ions in the plating solutions increases the NiP plating rate even more, due to the increased buffering capacity of solutions. An increase in nickel plating rate always is related to a decrease in P content in the coating and to an increase in the hypophosphite utilization efficiency. These effects are more pronounced if dicarboxylic acid of higher molecular weight is used as an additive.

**Key words:** electroless nickel, Cu^{2+} stabilizer, dicarboxylic acid

**INTRODUCTION**

Electroless nickel coatings have gained a good deal of popularity and acceptance in recent years as they provide considerable improvement of desirable properties. The plating process enables to deposit a uniform coating regardless of the shape of surface irregularities. Electroless nickel plating has been conducted in different baths to find optimum conditions for desirable properties, such as good corrosion and wear resistance, hardness and others [1–7]. The amount of phosphorus codeposited with nickel can affect the strength and wear properties of coatings. The P content can be changed under certain conditions of plating, such as composition and pH of the plating bath used.

An addition of some inhibitors may improve the stability of the plating bath, surface roughness of coatings, however, they frequently lower the NiP deposition rate. It has been established that a certain quantity of Cu^{2+} ions sufficiently stabilizes electroless nickel plating solution containing glycine as a ligand for Ni^{2+} ions, increases the NiP plating rate, improves coating appearance and ensures non-ferromagnetic stability [8]. Experiments of using Cu^{2+} in an acetate–citrate bath allowed proposing a model to explain the stabilizing role of Cu^{2+} ions by a partial reduction of them to the Cu^{+} state [9]. A positive action of the combination of Cu^{2+} with adipate was observed in an acidic citrate nickel plating solution [10]. It has been established that the deposition of smooth and bright nickel coatings in this case is determined by a stronger adipate interaction with NiPCu surface than with that of NiP [11].

The aim of the present work was to study peculiarities of electroless nickel plating in acidic solutions containing different ligands for Ni^{2+} ions and to elucidate the influence of adipic and other dicarboxylic acids present in these solutions along with Cu^{2+} ions.

**EXPERIMENTAL**

The NiP coatings were plated at a temperature of 85 °C in solutions containing (M): NiSO_4 - 0.1, NaH_2PO_2 - 0.25 and one of the ligands: Na acetate, Na citrate, glycine or lactic acid. Their concentrations necessary to bound 0.1 M Ni^{2+} were established spectrometrically (FEK 2). The concentrations of the additives used in the indicated cases were: CuSO_4 - 0.2 mM, dicarboxylic acid (malonic, succinic or adipic) - 0.1 M. Solution pH was adjusted to 4.5 at room temperature with NaOH and H_2SO_4.

NiP coatings were deposited during 1 h onto...
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...vated copper foil to determine the plating rate and buffering properties of solutions (1dm$^2$/l). Coatings of equal thickness (10 µm) were deposited onto roughened glass, to determine coatings composition and hypophosphite utilization efficiency.

The quantities of P and Cu after dissolution of coatings were detected photometrically with ammonium molybdate and diethyldithiocarbamate, respectively. The concentration of hypophosphite in the plating solution was determined by titration with ammonium vanadate [12]. Hypophosphite utilization efficiency was estimated as a ratio of its theoretical quantity necessary for the discharge of the Ni, P and Cu quantities detected in the coatings to a total sum of hypophosphite consumed in the process.

It has been accepted that the discharge of 1 M nickel or 1M copper requires 2M of hypophosphite while 1M phosphorus requires 4 M hypophosphite [13].

The data presented in Tables are the arithmetical mean of no less than three experiments.

**RESULTS AND DISCUSSION**

NiP plating without additives

Three reactions catalyzed by Ni and taking place simultaneously comprise the electroless plating process, which in a weak acidic solution may be described as follows [13]:

\[
\begin{align*}
2H_2PO_2^- + 2H_2O + Ni^{2+} & \rightarrow Ni + 2H_2PO_3^- + 2H^+ + H_2 \\
4H_2PO_2^- + H^+ + H_2O & \rightarrow 3H_2PO_3^- + P + 2.5H_2 \\
H_2PO_3^- + H_2O & \rightarrow H_3PO_4^- + H_2
\end{align*}
\]

The amount of the hypophosphite consumed in each of these reactions (at constant Ni$^{2+}$, H$_2$PO$_2^-$ concentrations, pH and temperature) depends on the nature of the ligand which determines the stability of a complex with Ni$^{2+}$, the buffering properties of
solution and other parameters. Therefore, a comparison of electroless nickel plating in solutions containing different types of organic acid (acetic, lactic, citric or glycine) ions as ligands along with \( \text{NiSO}_4 \) and \( \text{NaH}_2\text{PO}_2 \) was carried out first. According to the stability of complexes with \( \text{Ni}^{2+} \) they may be aligned as follows: acetate < lactate < citrate < glycinate [14]. Ligand concentrations necessary to bind 1 M \( \text{Ni}^{2+} \) ions were established on the basis of spectrometric measurements. Taking into account the data presented in Figs. 1–4, ligand concentrations for further investigations were chosen as follows (M): lactic acid 0.25, acetate 0.2, citrate 0.1, glycine 0.4.

As is shown in Table 1, the NiP plating rate from acetate solution was the highest and tended to diminish with an increase in the stability of the complex \( \text{Ni}^{2+} \text{–acid ions} \). It decreases drastically when glycine or citrate are used as ligands. It should be noted that citrate nickel plating solution is unstable under the studied conditions (as is also acetate plating solution) and may be used in practice only after its stabilization. Taking into account this circumstance, NiP coating deposition in citrate nickel plating solution could be somewhat easier. It is likely that the low NiP plating rate in the case of more complicated glycinate and citrate complexes is caused by difficulties related to their steric hindrance in hypophosphite adsorption and nickel discharge onto an active surface. A particularly strong adsorption of citrate onto the NiP surface, observed in our previous work [11], may support this presumption. According to the literature data, the hindering action of some additives on \( \text{Ni}^{2+} \) ions discharge from acetate nickel plating solution was arranged as follows: lactate < malonate < citrate < EDTA [15]. The fact that these additives may be aligned in the same manner according to their steric complexity is another point in favour of the steric hindrance. Strong adsorption of ligand ions onto NiP
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The presence of Cu$^{2+}$ ions essentially stabilizes all the nickel plating solutions studied and increases the plating rate by 7–15% (Table 1). An increase in nickel plating rate was attributed to the improved catalytic activity of the surface with Cu incorporated [19]. A similar increasing effect was also observed for Cd, Pb and S ions containing stabilizers at certain concentrations [20] and might be also attributed to qualitative changes in the nickel surface structure. The content of Cu in the coatings 10 µm thick varies from 0.8 to 1.3 wt.%, depending on the plating solution composition. A higher Cu quantity, similarly to that of phosphorus, is found in the coatings deposited at a lower rate.

The alteration in plating solution pH after deposition of 1 mg NiP in the presence of Cu$^{2+}$ ions is slightly higher as compared to that in the plating solutions without the additive (Table 1). A more pronounced decrease in solution pH after deposition of the same NiP quantity in the presence of Cu$^{2+}$ ions may confirm the earlier proposed model [9], whereby the adsorbed Cu$^{2+}$ ions are reduced equally into Cu$^{0}$ (codeposited in the alloy) and Cu$^{+}$ (acting as a stabilizer) by the following reactions:

\[
\text{Cu}^{2+} + 2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} \rightarrow \text{Cu} + 2\text{H}_2\text{PO}_3^- + + 2\text{H}^+ + \text{H}_2, \quad (4)
\]

\[
2\text{Cu}^{2+} + 2\text{H}_2\text{PO}_2^- + 2\text{H}_2\text{O} \rightarrow 2\text{Cu}^+ + 2\text{H}_2\text{PO}_3^- + + 2\text{H}^+ + \text{H}_2. \quad (5)
\]

These reactions occur only in the presence of active nickel surface, because Cu does not catalyze hypophosphite oxidation.

The hypophosphite utilization efficiency in the presence of Cu$^{2+}$ ions has a tendency to increase with an increase in the coating deposition rate and a decrease in the P content incorporated into the NiP surface.

### Table 2. Nickel plating parameters and coating composition depending on ligand concentrations.

| Solution composition (M): NiSO$_4$ 0.1, NaH$_2$PO$_2$ 0.25, adipic acid 0.1 and CuSO$_4$ 0.2 mM; pH 4.5 |
|-------------------------------|----------------|----------------|----------------|----------------|----------------|
| Ligand, M                     | Plating rate, µm/h | ∆pH for deposition of 1 mg NiP | Coating composition, wt. % | Hypophosphite utilization for reaction (3) efficiency mol/mol Ni | Hypophosphite utilization efficiency mol/mol Ni |
| Na acetate 0.1                | 11.7            | 0.0035         | 93.1           | 90.5           | 0.32           |
| Na acetate 0.3                | 12.3            | 0.0020         | 93.7           | 5.5            | 0.20           |
| Na acetate 0.6                | 12.3            | 0.0012         | 93.4           | 5.8            | 0.10           |
| Lactic acid 0.1               | 11.0            | 0.0053         | 93.5           | 5.8            | 0.12           |
| Lactic acid 0.2               | 11.0            | 0.0050         | 92.5           | 5.8            | 0.11           |
| Lactic acid 0.3               | 11.0            | 0.0050         | 92.5           | 5.8            | 0.11           |
| Glycine 0.2                    | 8.0             | 0.0043         | 91.5           | 5.6            | 0.27           |
| Glycine 0.4                    | 8.0             | 0.0043         | 90.5           | 5.8            | 0.31           |
| Glycine 0.6                    | 8.0             | 0.0043         | 90.5           | 5.8            | 0.31           |
| Na citrate 0.05                | 7.5             | 0.0027         | 90.7           | 4.0            | 0.55           |
| Na citrate 0.1                 | 7.5             | 0.0027         | 92.0           | 4.0            | 0.39           |
| Na citrate 0.3                 | 7.5             | 0.0027         | 92.0           | 4.0            | 0.39           |
| Na citrate 0.15                | 7.5             | 0.0027         | 92.0           | 4.0            | 0.39           |

The use of dicarboxylic acid additives increases the plating rate even more significantly when a dicarboxylic acid (malonic, succinic or adipic) takes part in the plating solution along with Cu$^{2+}$ ions. This increase (at equal acid concentrations) is proportional to the length of a –CH$_2$– chain in the dicarboxylic acid. The increase in plating rate is the highest when adipic acid is used, reaching 100% in the glycinate solution (in the other plating solutions – about 40%). An increase in...
plating rate is related to an improvement of solution buffering capacity and is proportional to the molecular weight of the dicarboxylic acid used.

No distinct changes are evident in the composition of coatings plated in the presence of dicarboxylic acid as compared to the coatings plated only with a Cu\(^{2+}\) ion additive. Some tendencies in the decrease of P and Cu quantities, observed in the presence of dicarboxylic acids are probably related to the increase in the nickel plating rate.

The consumption of hypophosphite in the catalytic reaction with water (3) is lower, thereby hypophosphite utilization efficiency is higher in the presence of dicarboxylic acid independently on its nature. One more advantage of using them (especially adipic acid) along with Cu\(^{2+}\) ions is an improvement in coatings’ appearance, because they become brighter and smoother.

Table 2 shows that no distinct changes were observed in the nickel plating parameters either with an increase or decrease in acetate or lactate concentrations in the solutions containing Cu\(^{2+}\) ions and adipic acid. At the same time, an increase in glycate or citrate concentrations in corresponding solutions leads to a significant decrease in nickel plating rate, particularly in citrate solution. With the increase in glycate or citrate concentrations the P and Cu quantities in the coatings first increase to some extent, however, with a subsequent increase in ligand concentrations the composition of the coatings remains practically identical. A more considerable increase in Cu quantity is observed at a higher citrate concentration in the solution when the plating rate decreases drastically. The decrease in hypophosphite utilization efficiency with the increase in glycate and citrate concentrations in the nickel plating solutions is proportional to the decrease in nickel plating rate. Therefore, steric and adsorption hindrances of ligand ions significantly affecting the Ni\(^{2+}\) ion discharge apparently less affect the other two reactions taking place simultaneously.

CONCLUSIONS

1. The reaction of nickel discharge from more complicated complexes is more significantly hindered by steric and adsorption factors than the other reactions catalyzed by nickel, that simultaneously take place in the electroless plating solution. Therefore, a decrease in nickel plating rate is related to an increase in the quantity of P incorporated into the coating and to a decrease in the hypophosphite utilization efficiency.

2. 0.2 mM Cu\(^{2+}\) sufficiently stabilizes all the electroless nickel plating solutions studied and to some extent increases the plating rate. The quantity of Cu incorporated into the coatings 10–15 \(\mu\)m thick varies in the range 0.8 to 1.3 wt.% depending on the plating conditions.

3. The ability of dicarboxylic acids (malonic, succinic, adipic) to increase the nickel plating rate is proportional to their molecular weight and is related to an improvement of the solution buffering capacity. The presence of dicarboxylic acid along with Cu\(^{2+}\) ions in the plating solution increases the hypophosphite utilization efficiency.

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Cu\(^{2+}\) IR DIKARBOKSIRUGDĖIØ ATAKA CHEMINIAM NIKELIO DANGØ NUSODINIMUI

Santrauka

Nikelio dangos buvo nusodinamos 85°C temperatūroje hipofosfitu tirpaluose, kuriuose Ni\(^{2+}\) jonams ligandais buvo
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acetatas, citratas, pieno rūgūdis arba glicinas. Tirpalø pH iki 4,5 buvo reguliuojamas kambario temperatūroje. Nustatyta, kad dangø nusédimo greitis tuo mažesnis, o fosforo kiekis jose tuo didesnis, kuo patvaresnis Ni\textsuperscript{2+} – organinės rūgūties jonø kompleksas. Ypač lėtai nusodinamos dangos tirpaluose, kuriuose ligandais yra glicinas arba citratas. Manoma, kad Ni\textsuperscript{2+} jonø išsikrovimà apsunkina ðiø kompleksø erdviniai faktoriai bei įenklesnė laisvø ligando jonø adsorbicija ant aktyvaus NiP pavirðiaus.

0,2 mM CuSO\textsubscript{4} pakankamai gerai stabilizuojà visus tirtus cheminio nikeliavimo tirpalus ir greitina dangø nusodinimà. Ā dangàs áiterpia 0,8–1,3 sv.\% Cu. K artu su Cu\textsuperscript{2+} jonas pridëjus anikeliavimo tirpalà dikarboksirūgūties (malono, gintaro arba adipino) dangø nusédimas dar labiau pagreitëja, padidëjus tirpalø buferinëi talpai. Nikelio dangø nusédimo pagreitëjimas yra susijàs su fosforo kiekio jose sumaþëjimu bei efektyvesniu hipofosfito sunaudojimu. Ðie efektai ryðkesni, kai á tirpalà при- dedama didesnio molekulinio svorio dikarboksirūgūties.