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INFLUENCE OF ORGANIC LIGANDS ON COPPER ELECTRODEPOSITION FROM MONO- AND POLYLIGAND ELECTROLYTES

V.M. Artemenko, A.O. Maizelis. Вплив органічних лігандів на електроосадження міді з моно- та полілігандних електролітів. Виявлення закономірностей електровиділення міді з низькоконцентрованих електролітів, що містять різні ліганди, важливе, оскільки вони моделюють складові різних мідь-вмісних рідких відходів та електролітів для осадження сплавів міді з більш електронегативними металами. **Мета:** Метою роботи є визначення характеристики електроосадження міді з деяких низькоконцентрованих моно- і полілігандних електролітів, які містять органічні ліганди. **Матеріали і методи:** Розглянуто електроліти, що містять як неорганічні (аміак і пірофосфат), так і органічні (тарtrat, етилендіамінтетраацетат, гліцинат, сульфосаліцилат) ліганди. Електроосадження міді досліджено потенціодінамічним методом. Розсічу здатність електролітів визначали за допомогою комірки Хула. **Результати:** Показано, що електроосадження міді у присутності органічних лігандів (тартрату, етилендіамінтетраацетату, гліцинату та сульфосаліцилату) відбувається з більш високою поляризацією та поляризуемістю, в порівнянні з сульфатним електролітом, що призводить до осадження дрібнозернистого та однорідного покриття. Величина поляризації і поляризуемості під час катодного осадження міді з полілігандного електроліту, що містить амоній і гліцин, мають середні значення між величинами поляризації і поляризуемості при виділенні міді з монолігандних електролітів (аміачного і гліцинатного). Додавання динатрієвої солі етилендіамінтетраоцетової кислоти у пірофосфатний електроліт міднення призводить до деполаризації процесу відновлення міді. Додавання сульфосаліцилату як додаткового ліганду збільшує утруднення розряду міді за рахунок повільної попередньої хімічної стадії, що передуює стадії розряду змішаних комплексів. Низькоконцентрований полілігандний електроліт на основі змішаних пірофосфатно-сульфосаліцилатних комплексів може бути рекомендований для електроосадження мідного підшару на основу, що має більш електронегативний потенціал.

Ключові слова: мідь, електроосадження, аміак, пірофосфат, сульфосаліцилат, гліцинат, тарtrat.

V.M. Artemenko, A.O. Maizelis. Influence of organic ligands on copper electrodeposition from mono- and polyligand electrolytes. It is important to know the laws of copper electrodeposition from low-concentrated electrolytes containing different ligands because they simulate components of various copper-containing liquid wastes and electrolytes for electrodeposition of copper alloys with more electronegative metals. **Aim:** The aim of the research is to determine the characteristics of copper electrodeposition from low-concentrated mono- and polyligand electrolytes containing organic ligands. **Materials and Methods:** Electrolytes containing both inorganic (ammonia and pyrophosphate) and organic (tartrate, ethylenediaminetetraacetate, glycinate, sulfosalicylate) ligands were considered. Throwing power of electrolytes was determined using Hull cell. **Results:** It is shown that the copper electrodeposition in the presence of organic ligands occurs with high polarization and polarizability in comparison with sulphate electrolyte that leads to the deposition of fine-grained and uniform coating. The values of polarization and polarizability during cathodic copper electrodeposition from polyligand electrolyte containing ammonium and glycinate are between the values of polarization and polarizability during cathodic copper electrodeposition from monoligand (ammonia and glycinate) electrolytes. The addition of ethylenediaminetetraacetic acid disodium salt to copper pyrophosphate electrolyte leads to the depolarization of the copper reduction process, while addition of sulfosalicylate as additional ligand increases the copper discharge complications due to the delayed prior chemical stage of complex dissociation. The low-concentrated polyligand electrolyte based on the mixed pyrophosphate-sulfosalicylate complexes can be recommended for electrodeposition of copper underlayer on the substrate with electronegative potential.

Keywords: copper, electrodeposition, ammonia, pyrophosphate, sulfosalicylate, glycinate, tartrate.

Introduction. Interest in low-concentrated electrolytes for copper electrodeposition is based on the necessity of determination of cupric ions reduction conditions during copper electrowinning from waste waters, or regeneration of copper-containing wastes [1...3] e.g. solutions for copper removing from details surface after gas cementation, or selective treatment of number of electrolytes from cupric ions contaminants. Preliminary studies have shown the effectiveness of maintenance of metal ions concentration in modified galvanic drag-out baths at the level of 2...3 g dm⁻³ for both electrolysis and rinse-water baths operation [4]. In addition, electrolytes with low concentration of cupric ions are used in printed circuit boards production [5], and in electrodeposition of copper alloys [6...9].

The aim of the research is to determine the characteristics of copper electrodeposition from low-concentrated mono- and polyligand electrolytes containing organic ligands.

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Materials and Methods. The cathode processes was studied by analyzing of voltammograms obtained on the copper electrodes. All measurements were performed in three-electrode cell using potentiostat PI-50.1. The working electrodes (10 mm×10 mm) were made of copper pressed in fluoropolymer. All of the samples were sanded with silicon carbide paper (500, 1000, 2000 and 3000 grit). The saturated silver chloride electrode was used as a reference electrode. All potentials shown in the figures are against this electrode. The potential scan rate was 50 mV s⁻¹. The results of measurements were sent to PC using dual-channel voltmeter and “TeleMax” application at the rate of 20 signals per second. The coatings were deposited using stabilized power supply B5-43. All solutions were prepared using chemicals of “chemically pure” qualification. The pH of the solutions was determined using the pH-meter pH-150. The changes of electrode masses were fixed using analytical scales VLR-200. The photos of surface morphology of the coatings were obtained using microhardness tester PMT-3 and digital camera Canon PowerShot A1100 IS. Throwing power of electrolytes was determined using Hull cell. The compositions of the studied low-concentrated electrolytes are listed in Table 1. The pH of all solutions was 8.5, except sulphate electrolyte, where pH was not corrected. The selected value of ligands concentration corresponds to the formation of stable solutions with minimal ligands content at the mentioned pH. Free copper ions were almost absent in the solutions, since they were transparent at pH 8.5, i.e. at the higher pH, than the value of pH of hydrate formation is.

Table 1

Composition of the solutions for copper electrodeposition

Electrolyte		Component contents, mol dm ⁻³							
		[Cu ²⁺]	[P ₂ O ₇ ⁴⁻]	[NH ₃]	[SSal ³⁻]	[Gly ⁻]	[Y ⁴⁻]	[Tart ²⁻]	[Na ₂ SO ₄]
1	Sulfuric	0.05	–	–	–	–	–	–	0,3
2	EDTAcetate (Y ⁴⁻)	0.05	–	–	–	–	0.05	–	–
3	Glycinate (Gly ⁻)	0.05	–	–	–	0.05	–	–	–
4	Tartrate (Tart ²⁻)	0.05	–	–	–	–	–	0.15	–
5	Ammonia (NH ₃)	0.05	–	0.3	–	–	–	–	–
6	Ammonia-Glycinate	0.05	–	0.15	–	0.15	–	–	–
7	Pyrophosphate-Sulfosalicylate (P ₂ O ₇ ⁴⁻ -SSal ³⁻), high-concentrated	0.3	1	–	0.25	–	–	–	–
8	Pyrophosphate	0.05	0.3	–	–	–	–	–	–
9	Pyrophosphate-EDTAcetate	0.05	0.15	–	–	–	0.025	–	–
10	Pyrophosphate-Sulfosalicylate	0.05	0.15	–	0.04	–	–	–	–

Results and Discussion.

Investigation of cathodic process in sulfate electrolyte. Polarization curve of copper electrodeposition from high-concentrated [10] sulphate electrolyte (Fig. 1, curve 1) shows the cupric ions reduction with low overpotential and electrolyte polarizability, resulting in electrodeposition of coatings with large-scale crystals. The rate of contact deposition of copper on details made of steel is high in this electrolyte, which leads to the low adhesion of coating to substrate.

The polarization curve for the cupric ions reduction from low-concentrated sulphate solution (Table 1, electrolyte 1) can be divided into three regions (Fig. 1, a, curve 2). In the first part of the curve (region of potentials before –0.25 V), the current density increases from 0 to 0.6 A dm⁻² and copper can be deposited in the form of dense coating. The second part of the curve (from –0.25 to –0.75 V) corresponds to the limiting current and the quality of copper deposits deteriorates due to formation of dendrites. At the third part of the curve (more negative potentials than –0.75 V) the rate of hydrogen evolution increases, that leads to the deposition of copper in the form of powder.

Overpotential of cupric ions reduction from low-concentrated electrolyte is higher than from the high-concentrated solution. This improves the coating structure, but such overpotential is not high enough for direct copper electrodeposition on steel substrate.

Investigation of cathode processes in monoligand electrolytes containing copper complexes with organic ligands. The main criteria for selecting ligands were their non-toxicity, stability of complex compounds and solutions. Among organic ligands, the tartrate ions, EDTAcetate, glycinate, sulfosalicylate ions (instability constants of copper complexes are $1.4 \cdot 10^{-10}$, $1.6 \cdot 10^{-19}$, $1.35 \cdot 10^{-7}$, $5.4 \cdot 10^{-10}$ respectively [11]) are the best-suited to such requirements.

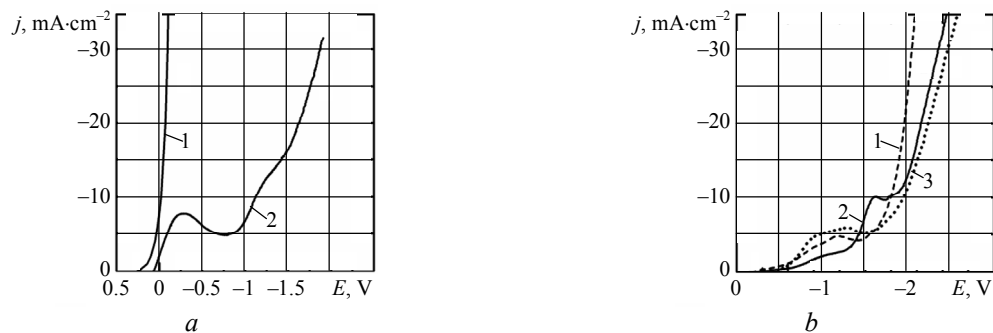


Fig. 1. Cathodic polarization curves in electrolytes: 1a – high-concentrated sulfate, 2a – low-concentrated sulfate, 1b – tartrate, 2b – EDTAcetate, 3b – glycinate

At the potentials of compact copper coating deposition (from -0.5 to -1 V) the lowest deposition rate was observed in EDTAcetate electrolyte (Fig. 1, b, curve 2; Table 1, electrolyte 2), and the highest rate was found out in glycinate electrolyte (curve 3, electrolyte 3). The value of the rate of copper electrodeposition from tartrate electrolyte (curve 1, electrolyte 4) is between the rate values in other mentioned electrolytes, despite the highest content of ligand. This fact is in a good agreement with the value of copper complexes stability constants and the charge value of the prevail particles in the solutions (CuGly_2 [12], $\text{Cu}(\text{Tartr})_2(\text{OH})_2^{4-}$ [13], chelate CuY^{2-}). Copper electrodeposition from all three solutions is accompanied by high polarization and polarizability that promotes deposition of fine-grained and uniform coating. Shifting of the electrodeposition potential promotes reduction of contact exchange rate when using these electrolytes for electrodeposition of copper coating on steel substrate.

Cathodic processes in electrolytes containing copper complexes with ammonia and glycine. Due to the formation of fairly strong complex copper compounds with ammonia (instability constant is $2.14 \cdot 10^{-13}$ [11]), copper deposits in the form of fine-grained coatings from ammonia electrolyte. The significant disadvantage of this electrolyte is its low stability during operation. The adhesion between substrate and coating electrodeposited from this electrolyte is also not high enough. We considered the possibility of improving of coating properties and technological characteristics of the electrolyte with combination of two ligands (glycinate and ammonia) in one solution.

The cathodic polarization curves of copper electrodeposition from ammonia (curve 1, electrolyte 5), glycinate (curve 3, electrolyte 3) and mixed ammonia-glycinate (curve 2, electrolyte 6) electrolytes are shown in Fig. 2. The equilibrium potential of copper-ions in ammonia solution is more positive than potentials in the other two electrolytes. In addition, this electrolyte is characterized by the lowest cathodic polarization. The values of polarization and polarizability during cathodic copper electrodeposition from polyligand electrolyte containing ammonium and glycinate are in between the values polarization and polarizability during cathodic copper electrodeposition from monoligand (ammonia and glycinate) electrolytes.

As it is noted in [14], copper complexes with two glycine zwitterions (CuGly_2) are formed in the excess of glycine. In the absence of this excess, the fraction of the copper complex with one zwitterion (CuGly^+) increases in the absence of this excess, under conditions of other ions competition. It is

possible that the increase in the particles charge at the negative cathode is related to decrease of complications of copper deposition in the mixed electrolyte compared with glycinate electrolyte. So we can assume, that the rate of contact exchange when using glycinate and mixed ammonia-glycinate electrolytes is lower than in ammonia electrolyte, while using the details loading under the operating current density will decrease the contact exchange.

Cathodic processes in pyrophosphate electrolytes in the presence of additional organic ligands. The monoligand pyrophosphate electrolytes are moderately used in the industry as alternative to cyanide, but they could not compete with the latter by the technological characteristics. In order to improve the structure of copped electrodeposits from pyrophosphate electrolytes, their thickness uniformity and improve anode process, the polyligand electrolyte based on mixed sulfosalicylate-pyrophosphate complexes was developed [15].

The throwing power (Fig. 3) of high-concentrated pyrophosphate-sulfosalicylate electrolyte (electrolyte 7) is higher compared to high-concentrated sulphate electrolyte (curve 1). The throwing power was measured at operating current density for each electrolyte. It should be noted that more uniform coatings can be deposited at a lower current density from the low-concentrated pyrophosphate-sulfosalicylate electrolyte (curve 3).

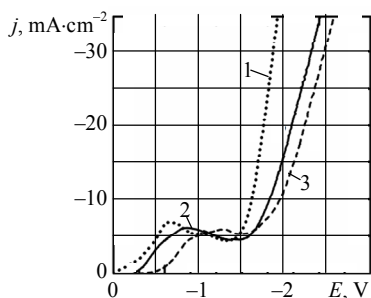


Fig. 2. Cathodic polarization curves in electrolytes:
1 – ammonia, 2 – mixed ammonia-glycinate,
3 – glycinate

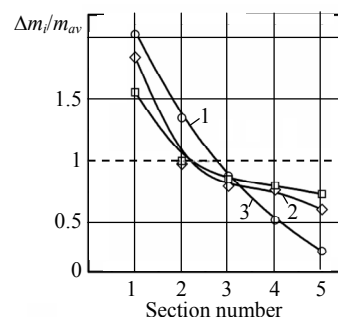


Fig. 3. Throwing power of high-concentrated sulphate (1), high-concentrated pyrophosphate-sulfosalicylate (2) and low-concentrated pyrophosphate-sulfosalicylate (3) electrolytes at a current density of 30 (1), 15 (2) and 10 mA/cm² (3)

The photos of the surface of sectional cathode of the Hull cell illustrate the deteriorating in the quality of copper coating on the sections that are located closer to the anode (Fig. 4).

The ratio of maximum and minimum overweight of the copper deposit from the high-concentrated pyrophosphate-sulfosalicylate electrolyte is reduced by 1.4 times compared to sulphate electrolyte and this ratio for low-concentrated pyrophosphate-sulfosalicylate electrolyte is reduced by 1.5 times compared to high-concentrated one. Therefore the pyrophosphate-sulfosalicylate electrolyte can be used for complex contoured details geometry, and the copper layer thickness can be reduced on the parts of plain configuration.

The electrodeposition of copper from low-concentrated pyrophosphate electrolyte (electrolyte 8), low-concentrated pyrophosphate electrolyte containing sulfosalicylate-ion additive (electrolyte 9) and pyrophosphate electrolyte with other additional ligand – EDTAcetate (electrolyte 10) was also studied.

The polarization curves in polyligand electrolytes, EDTAcetate-pyrophosphate (curve 1) and pyrophosphate-sulfosalicylate (curve 4), in comparison with monoligand electrolytes, pyrophosphate (curve 2) and EDTAcetate (curve 3, electrolyte 2), are presented in Fig. 5. The influence of the organic ligand on the copper electrodeposition from pyrophosphate electrolyte at the beginning of the curve is absent. At more negative potentials the polarization of copper electrodeposition is more significant in pyrophosphate-EDTAcetate electrolyte, then in other monoligand EDTAcetate electrolyte.

The polarization and polarizability of copper electrodeposition is higher in pyrophosphate-sulfosalicylate electrolyte in comparison with pyrophosphate electrolyte. However, the rate of copper electrodeposition from pyrophosphate-EDTAacetate and pyrophosphate electrolytes is much higher than from polyligand electrolyte containing sulfosalicylate ions. The pyrophosphate ion is polydentate ligand of acid type. Furthermore, it is a ligand of a weak field. Therefore, it does not interfere with the addition of other ligands and forms mixed compounds with a large number of coordination groups. The effect of these additional ligands on the electrochemical behaviour of complexes depends on the nature of the additional ligand. The higher complications in the copper deposition from the pyrophosphate-sulfosalicylate complex are apparently related to the ability of the additional ligand-sulfosalicylate to bind the central atom to cyclic group with the combined participation of phenolic and carboxyl groups and with discharge complications caused by the presence of a preliminary stage of dissociation of mixed complexes of $\text{Cu}(\text{C}_6\text{H}_3\text{OHCOOSO}_3)_2\text{P}_2\text{O}_7^{6-}$ [15].

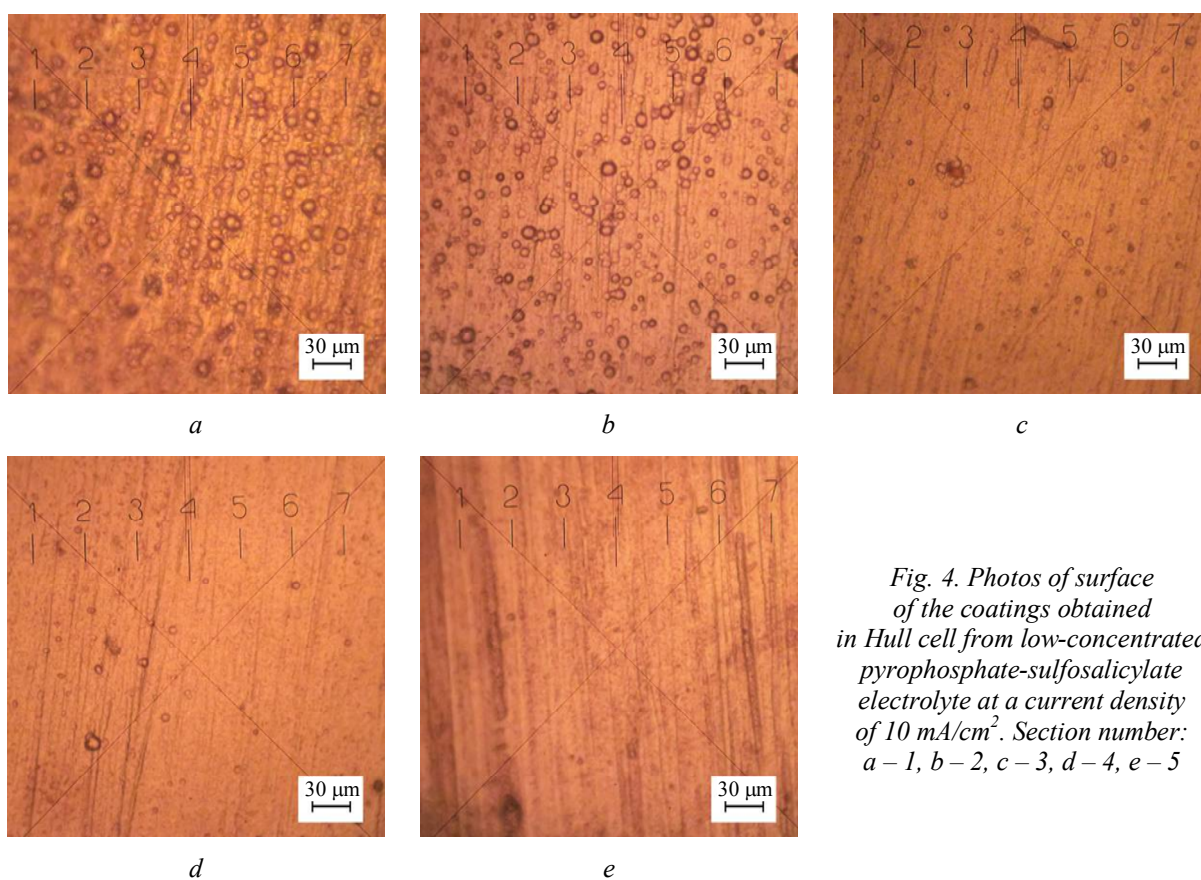


Fig. 4. Photos of surface of the coatings obtained in Hull cell from low-concentrated pyrophosphate-sulfosalicylate electrolyte at a current density of 10 mA/cm^2 . Section number: a – 1, b – 2, c – 3, d – 4, e – 5

The copper electrodeposition from low-concentrated pyrophosphate-sulfosalicylate electrolyte (Fig. 6) is characterized by lower working current density and higher polarization and polarizability, compared to high-concentrated electrolyte. This leads to the electrodeposition of uniform fine-grained copper coatings and reduces the probability of contact exchange between electrolyte and substrate made of steel to the limit. Therefore the low-concentrated polyligand pyrophosphate-sulfosalicylate electrolyte can be recommended as electrolyte for deposition of copper coatings on the substrate of more electronegative potential.

Conclusions. The electrolytes containing studied copper complexes with inorganic and organic ligands can be recommended as monoligand and polyligand systems along with other ligands. The copper electrodeposition in the presence of organic ligands occurs with high polarization and polarizability that leads to the deposition of fine-grained and uniform coating and to the reducing of contact exchange rate in the electrolytes.

The values of polarization and polarizability during cathodic copper electrodeposition from polyligand electrolyte containing ammonium and glycinate are between values polarization and polarizability during cathodic copper electrodeposition from monoligand (ammonia and glycinate) electrolytes.

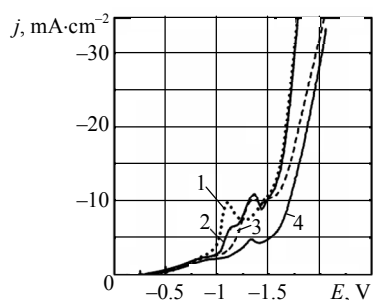


Fig. 5. Cathodic polarization curves in electrolytes: 1 – pyrophosphate-EDTAcetate, 2 – pyrophosphate, 3 – EDTAcetate, 4 – pyrophosphate-sulfosalicylate

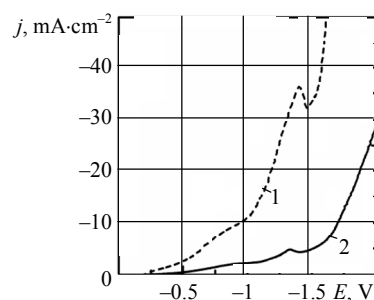


Fig. 6. Cathodic polarization curves in pyrophosphate-sulfosalicylate electrolytes: 1 – high-concentrated, 2 – low-concentrated

The influence of organic ligand on the copper electrodeposition from pyrophosphate electrolyte on the first part of the polarization curve was not found. At more negative potentials the depolarization of copper electrodeposition from pyrophosphate-EDTAcetate electrolyte was observed, while the greater polarization and polarizability of the process was observed in the pyrophosphate-sulfosalicylate electrolyte in comparison with pyrophosphate, which is associated with the complications caused by the presence of the previous stage of dissociation of mixed pyrophosphate-sulfosalicylate copper complexes.

The low-concentrated polyligand electrolyte based on the mixed pyrophosphate-sulfosalicylate complexes can be recommended for electrodeposition of the intermediate copper layer on the substrate made of more electronegative potential.

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