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D. P. THORZHEVSKY

Student at the Department of Electrochemical Productions Technology
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0009-0002-0455-1777

A. S. ZABALUEV

Assistant at the Department of Electrochemical Productions Technology
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0000-0002-9749-7599

D. YU. USHCHAPOVSKYI

PhD in Technical Sciences,
Associate Professor at the Department of Electrochemical Productions Technology
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0000-0002-2809-2774

V. I. VOROBYOVA

Doctor in Technical Sciences,
Head of the Department of Physical Chemistry Technology
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0000-0001-7479-9140

G. S. VASYLIEV

Doctor in Technical Sciences,
Associate Professor at the Department of Electrochemical Productions Technology
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0000-0003-4056-5551

O. V. LINYUCHEVA

Doctor in Technical Sciences,
Dean of the Chemical Technology Faculty
National Technical University of Ukraine
“Igor Sikorsky Kyiv Polytechnic Institute”
ORCID: 0000-0003-4181-5946

THE INFLUENCE OF ELECTROLYTE COMPOSITION ON THE CORROSION RESISTANCE OF NICKEL-BASED METAL-RESISTIVE COATINGS

This paper presents a study of the corrosion resistance of metal resistive nickel coatings and the influence of gloss-forming additives on it, which can be introduced into the electrolyte to improve the quality and uniformity of electroplated coatings.

Based on the conducted potentiodynamic polarization measurements and construction of corrosion diagrams, it has been shown that in a 3 % acetic acid solution, a 3 % sodium chloride solution, and a 3 % sodium chloride solution with the addition of 6 ml/l of acetic acid, the corrosion destruction of galvanic nickel deposits mainly occurs with cathodic control, and the limiting stage is, respectively, the stage of oxygen transport to the metal surface. It has been established that the corrosion destruction of nickel galvanic metal-resistive coatings in an alkaline copper-chloride solution for etching the conductive pattern of printed circuit boards occurs with mixed and predominant anodic control. It has been shown that due to the depassivating effect of inclusions of decomposition products of gloss-forming additives in the structure of nickel deposits, intensive destruction of the metal-resistive coating occurs in the environment of an alkaline copper-chloride solution for etching the conductive pattern of printed circuit boards. In the case of sulfur-free matte nickel deposits, contact with copper leads to a significant reduction in the corrosion rate, due to the possible stimulation

of passive film growth. This is also, to a much lesser extent, inherent in bright sulfur-containing coatings. It has been found that in order to apply corrosion-resistant nickel metal-resistive coatings, the use of sulfurogenic surfactants, such as saccharin, should be limited.

Key words: nickel plating, metal resistive coatings, acetic acid, sodium chloride, alkaline copper chloride etching solution, conductive pattern, corrosion resistance, passive film.

Д. П. ТХОРЖЕВСЬКИЙ

студент кафедри технології електрохімічних виробництв
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0009-0002-0455-1777

А. С. ЗАБАЛУЄВ

асистент кафедри технології електрохімічних виробництв
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0000-0002-9749-7599

Д. Ю. УЩАПОВСЬКИЙ

кандидат технічних наук,
доцент кафедри технології електрохімічних виробництв
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0000-0002-2809-2774

В. І. ВОРОБІЙОВА

доктор технічних наук,
завідувач кафедри фізичної хімії
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0000-0001-7479-9140

Г. С. ВАСИЛЬЄВ

доктор технічних наук,
доцент кафедри технології електрохімічних виробництв
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0000-0003-4056-5551

О. В. ЛІНЮЧЕВА

доктор технічних наук,
декан хіміко-технологічного факультету
Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського»
ORCID: 0000-0003-4181-5946

ВПЛИВ СКЛАДУ ЕЛЕКТРОЛІТУ НА КОРОЗІЙНУ СТІЙКІСТЬ МЕТАЛОРЕЗИСТИВНИХ ПОКРИТТІВ НА ОСНОВІ НІКЕЛЮ

У даній роботі представлено дослідження корозійної стійкості металореzystивних нікелевих покриттів та впливу на неї добавок блискоутворювачів, які можуть вводитись в електроліт з метою підвищення якості та рівномірності гальванічних покриттів.

На основі проведених потенціодинамічних поляризаційних вимірювань та побудови корозійних діаграм показано, що у 3 % розчині оцтової кислоти, 3 % розчині хлориду натрію, 3 % розчині хлориду натрію з додавання 6 мл/л оцтової кислоти, корозійне руйнування гальванічних нікелевих осадів переважно відбувається з катодним контролем, а лімітуючою є, відповідно, стадія транспорту кисню до поверхні металу. Встановлено, що корозійне руйнування нікелевих гальванічних металореzystивних покриттів у лужному мідно-хлоридному розчині травлення струмопровідного рисунку друкованих плат відбувається зі змішаним та переважним анодним контролем. Показано, що за рахунок депасивуючого впливу включень продуктів розкладу блискоутворювачів в структуру нікелевих осадів відбувається інтенсивне руйнування металореzystивного покриття в середовищі лужного мідно-хлоридного розчину травлення струмопровідного рисунку друкованих плат. У випадку безсульфоровмісних

матових нікелевих осадів контакт із міддю призводить до значного зменшення швидкості корозії, через можливе уцілювання пасивної плівки. Це також, значно в меншій мірі, притаманне блискучим сульфоровмісним покриттям. Виявлено, що з метою нанесення корозійностійких нікелевих металорезистивних покриттів слід обмежити використання сульфорогенних поверхнево-активних добавок, таких, як сахарин.

Ключові слова: нікелювання, металорезистивні покриття, оцтова кислота, натрію хлорид, лужний мідно-хлоридний розчин травлення, струмопровідний рисунок, корозійна стійкість, пасивна плівка.

Formulation of the problem

Metal-resistive coatings are used in the technology of printed circuit board production in order to create a current-conducting pattern. In the production of printed circuit boards, metal-resistive coatings are usually deposited from metals such as tin and its alloys, less often nickel. These metals have high corrosion resistance and stable total and surface conductivity. In particular, nickel coatings have high mechanical strength and wear resistance, which increases the durability of components on the boards [1, 2]. Increasing the protective properties and reducing the cost of deposition such coatings will contribute to the further development of the electronic, radio engineering and aviation industries.

Analysis of the latest research and publications

Nickel coatings in the technology of printed circuit board production are deposited as a sublayer before depositing gold or palladium coatings in order to reduce the transition resistance, increase mechanical properties and corrosion resistance. It is also important to note that nickel coatings are a cheaper alternative to tin coatings, which makes it economically feasible to replace the latter in the technological process of printed circuit board production [1–3].

In order to improve the quality and uniformity of nickel coatings, brighteners, in particular saccharin, are introduced into electrolytes. The latter is a source of sulfur, which is incorporated into the coating structure during electrodeposition [4–6]. Saccharin, as an organic compound, can be incorporated into the coating structure both through physical adsorption of molecules and through electrochemical reduction to metal sulfides [7]. The concentration of saccharin in the electrolyte significantly affects the characteristics of the coatings. At low concentrations (< 2 g/l), saccharin contributes to the formation of thin, homogeneous coatings with improved mechanical properties, in particular, with a smaller number of defects and cracks. At the same time, at high concentrations ($> 2,5$ g/l), the coating can become porous due to oversaturation of the solution with saccharin, which reduces its mechanical strength and corrosion resistance [7]. The inclusion of sulfur through saccharin negatively affects the corrosion resistance of coatings. High sulfur content reduce the corrosion resistance of coatings due to the formation of galvanic pairs between different phases, in particular sulfides. This leads to localized corrosion and degradation of the coating [8]. Excessive increase in the concentration of saccharin leads to a deterioration in corrosion resistance due to the formation of a porous coatings [7].

Formulation of the purpose of the research

Thus, the purpose of this work is to study the influence of the electrolyte composition, in particular, the content of gloss-forming additives, on the corrosion resistance and protective properties of nickel metal-resistive coatings, as well as to assess the possibilities of their use as metal-resistive coatings in corrosive and aggressive environments, and, in particular, in conditions of etching of conductive patterns of printed circuit boards.

Presentation of the main research material

Research methodology. At the initial stage, nickel-based materials were studied, for this purpose foil electrodeposition was carried out. For this purpose, industrial electrolytes were selected, the composition of which is given in Table 1.

Table 1

Nickel plating electrolytes and foil electrodeposition modes

Electrolyte composition, g/dm ³		
№ 1 (bright nickel plating on rack)	№ 2 (bright nickel plating in the barrel)	№ 3 (matte nickel plating on rack)
NiSO ₄ · 7H ₂ O – 250...300; NiCl ₂ · 6H ₂ O – 40...60; H ₃ BO ₃ – 30...40; Butynediol 35 % solution – 0.5...1.5 ml/l; Saccharin – 0,5...1	NiSO ₄ · 7H ₂ O – 250...300; NiCl ₂ · 6H ₂ O – 40...60; H ₃ BO ₃ – 30...40; Saccharin – 2...6	NiSO ₄ · 7H ₂ O – 250...300; NiCl ₂ · 6H ₂ O – 40...60; H ₃ BO ₃ – 30...40
Electrolysis mode		
pH 4...4,5; $t = 50 \pm 3$ °C; $i = 2...3$ A/dm ²	pH 4...4,5; $t = 50 \pm 3$ °C; $i = 2...3$ A/dm ²	pH 4...4,5; $t = 50 \pm 3$ °C; $i = 2...3$ A/dm ²
Sulfur content in the galvanic deposit, wt. %		
0,074	0,240	0,010>

For the purpose of electrodeposition of nickel foil, samples of AISI 321 stainless steel were used as a working electrode (cathode). The thickness of the resulting nickel foil was about 50 μm. To determine the sulfur content in electrolytic deposits, X-ray fluorescence analysis was used using an express analyzer of the “EXPERT 3L”. The results of determining the sulfur content in the foil are presented in Table 1.

Four solutions were used for polarization and corrosion tests: 3 % acetic acid (CH_3COOH); 3 % sodium chloride (NaCl); 3 % sodium chloride with the addition of 6 ml/l acetic acid; alkaline copper chloride solution for etching conductive patterns of printed circuit boards, the composition of which is close to that given in [3]. Distilled water and reagents of chemical grade were used to prepare the solutions. Due to the presence of volatile components in the tested solutions, such as ammonia and acetic acid, in order to create the same conditions for trapping the vapors of the corresponding compounds and entering air to the corrosive environment, gravimetric corrosion tests were carried out in desiccators with a capacity of 8 dm³. A separate desiccator was used for each of the solutions. Three polypropylene glasses with a capacity of 150 ml were loaded into each desiccator. The area of electrodeposited nickel foil samples was 3,6 cm². In order to study the influence of the copper substrate on the corrosion of nickel coatings, a fragment of copper foil with a thickness of 0,5 mm and an area of 0,5 cm² was attached to the nickel foil sample. The duration of exposure of samples during corrosion tests in the studied environments was 24 hours. Weighing of samples after washing and drying with warm air was carried out on the AS 220.R2 analytical balances, with a weighing accuracy of up to 10⁻⁴ g. The values of corrosion rate established by the gravimetric method were converted into a current indicator of corrosion rate.

The corrosion behavior of galvanic nickel deposits was studied by linear polarization using a digital potentiostat PGstat 500n in a standard three-electrode electrochemical cell with an auxiliary platinum electrode. The potential scanning rate during the obtaining of potentiodynamic polarization curves was 2 mV/s. The potentials on the curves are given in the scale of a saturated silver-chloride electrode. Based on the obtained polarization curves, corrosion diagrams were built, from which the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were determined. In order to assess the controlling reaction of the corrosion process, the values of the cathodic and anodic polarizations corresponding to i_{corr} were determined.

The study of the protective properties of metal-resistive coatings was carried out in an alkaline etching copper-chloride solution, which is used for chemical etching of conductive patterns of printed circuit boards. The samples used for the investigation were fragments of industrial printed circuit boards that had undergone the stages of preliminary galvanic copper plating and photoresist application on the blank areas. Nickel metal-resistive coatings with a thickness of 9 μm were electrodeposited into the photoresist windows on the conductive pattern after galvanic copper plating. The morphology of the resulting metal-resistive coatings on the conductive pattern was studied using an optical metallographic microscope MIM-7 equipped with a digital camera SIGETA USMOS08000KPB in the ToupView software.

Results of experimental studies. In order to study the corrosion behavior of galvanic nickel deposits, polarization measurements were carried out, on the basis of which corrosion diagrams were constructed, which are presented in Fig. 1, and the main electrochemical parameters of the corrosion process were determined (Table 2).

In general, from Fig. 1 *a, b, c*, and Table 2 it is seen that in acetic acid and sodium chloride solutions, corrosion destruction of bright galvanic nickel deposits (obtained from electrolytes № 1, № 2) mainly occurs with cathodic control, and the limiting stage is the stage of oxygen transport to the metal surface. For matte nickel, the control is mixed. In contrast, in an alkaline copper-chloride etching solution (Fig. 1. *d*), corrosion destruction of bright and matte nickel foil occurs mainly with mixed and anodic control. Thus, the high passivation ability and the presence of a dense passive film, which is present precisely on matte nickel deposits obtained from electrolytes without gloss formers (saccharin), make the main contribution to the metal-resistive properties of the coatings as a whole.

Comparison of the results of determining the corrosion rate by the gravimetric method and the polarization curve method (based on Fig. 1) shows approximately the same susceptibility of nickel foil samples to corrosion destruction (Fig. 2). Higher values of corrosion rates determined from polarization curves are explained by the influence of the potential scanning rate on the course of the polarization curve. In general, it is seen that in NaCl solution the corrosion rate of the studied nickel foil samples is the lowest and almost the same. In solutions containing acetic acid, as well as in alkaline copper chloride solution, the corrosion rate for bright nickel foil samples (obtained from electrolytes № 1 and № 2) was significantly higher than for matte sulfur-free foil (electrolyte № 3).

In addition to nickel foil samples, in order to simulate the presence of nickel metal resist on the surface of the conductive pattern of the printed circuit board, gravimetric corrosion tests were carried out for galvanic couples, which were created from fragments of nickel and copper foil. Comparing the data in Fig. 2 and 3, the following conclusions can be made. In acetate-containing solutions and sodium chloride solutions, the presence of contact between nickel and copper in the studied corrosive environments generally causes a decrease in the corrosion rate. Such an inhibitory effect of contact with copper can be explained as follows. On the one hand, copper, as a more electropositive metal, can impose its potential and cause the compaction of the passive film on nickel, which will mainly concern matte sulfur-free foil. On the other hand, the possible copper-stimulated dissolution of the bright foil at the initial point in time can cause blocking of the metal surface with poorly soluble corrosion products, and, as a result, inhibit the process of corrosion destruction. In an alkaline copper-chloride etching solution, copper can generally act as a protector – creating cathodic protection for nickel.

Nickel coatings were electrodeposited onto the surface of the conductive pattern of printed circuit boards, after which the conductive pattern was etched in an alkaline copper chloride solution in order to test the metal-resistive properties of the studied coatings (Fig. 4). It was found that when electrodepositing bright nickel coatings obtained from electrolytes

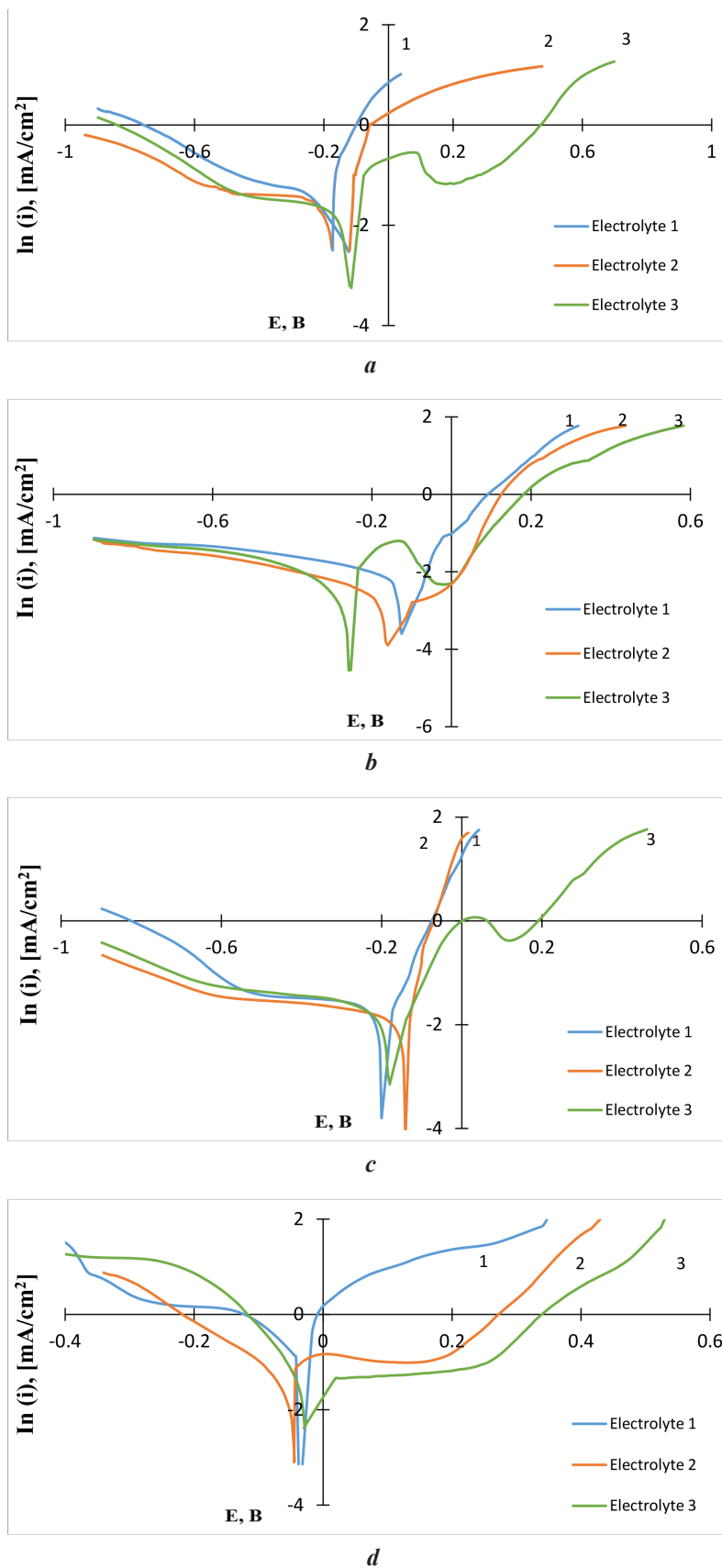


Fig. 1. Corrosion diagrams for the studied nickel foil samples in: *a* – 3 % CH_3COOH ; *b* – in 3 % NaCl ; *c* – 3 % NaCl with the addition of 6 ml/l CH_3COOH ; *d* – in alkaline copper chloride etching solution

Table 2

Electrochemical parameters of corrosion processes for nickel foil samples

Solution	№ electrolyte	Corrosion current, $\lg(i_{corr})$, [mA/cm ²]	Corrosion potential, E_{corr} , V	ΔE_a , V	ΔE_k , V
3 % CH ₃ COOH	1	-1,4	-0,173	0,010	0,177
	2	-1,48	-0,120	0,008	0,130
	3	-1,6	-0,120	0,020	0,110
3 % NaCl	1	-2,1	-0,120	0,035	0,080
	2	-2,4	-0,160	0,080	0,090
	3	-2,4	-0,253	0,010	0,060
3 % NaCl + 6 ml/l CH ₃ COOH	1	-1,6	-0,198	0,020	0,060
	2	-1,7	-0,130	0,008	0,080
	3	-1,8	-0,180	0,040	0,080
Etching copper-chloride solution	1	-0,8	-0,040	0,008	0,008
	2	-1,1	-0,019	0,060	0,030
	3	-1,35	-0,050	0,060	0,020

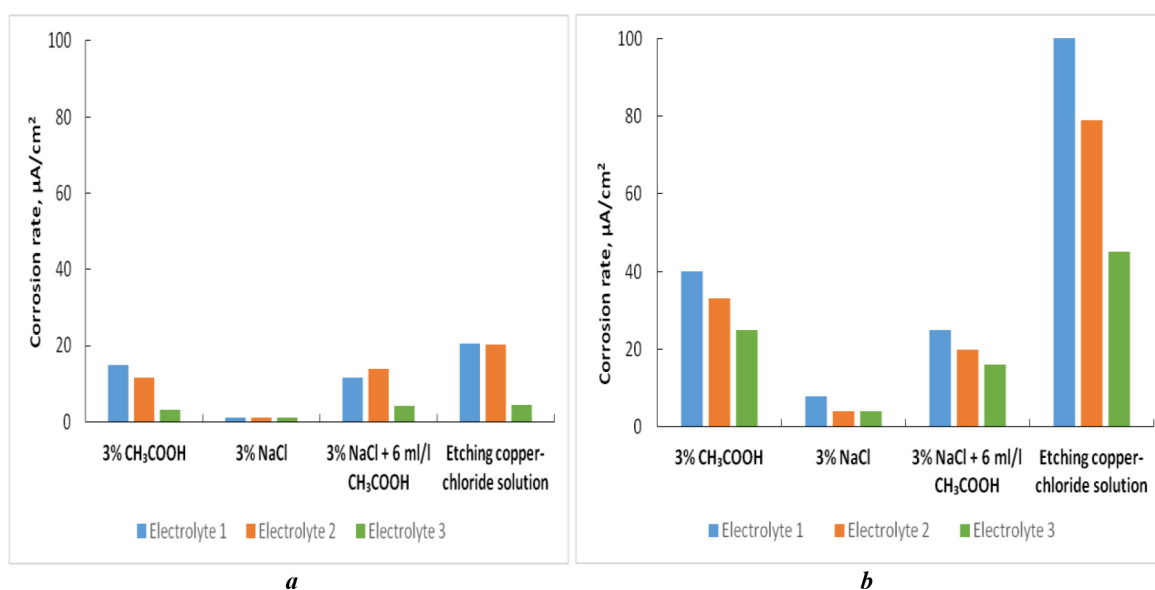


Fig. 2. The influence of the composition of the electrolyte for the deposition of nickel resist on its corrosion resistance, determined by gravimetric (a) and the method of corrosion diagrams (b)

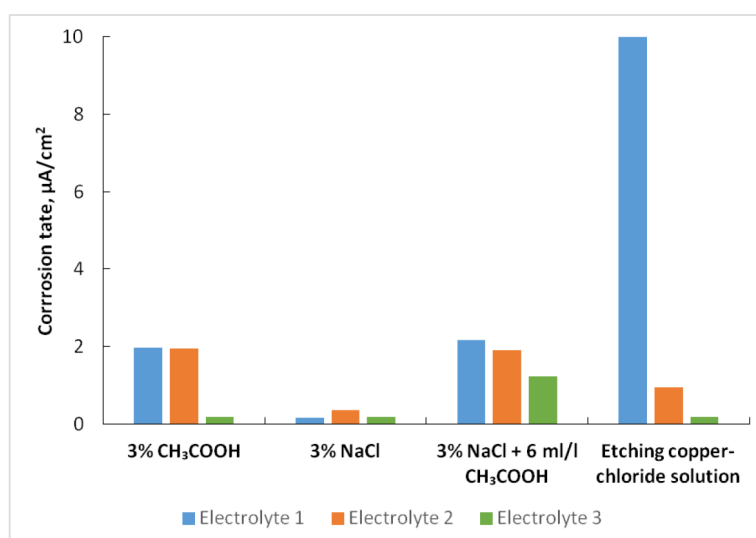


Fig. 3. Corrosion rate values of nickel foil samples during the formation of galvanic couple with copper, obtained by the gravimetric method

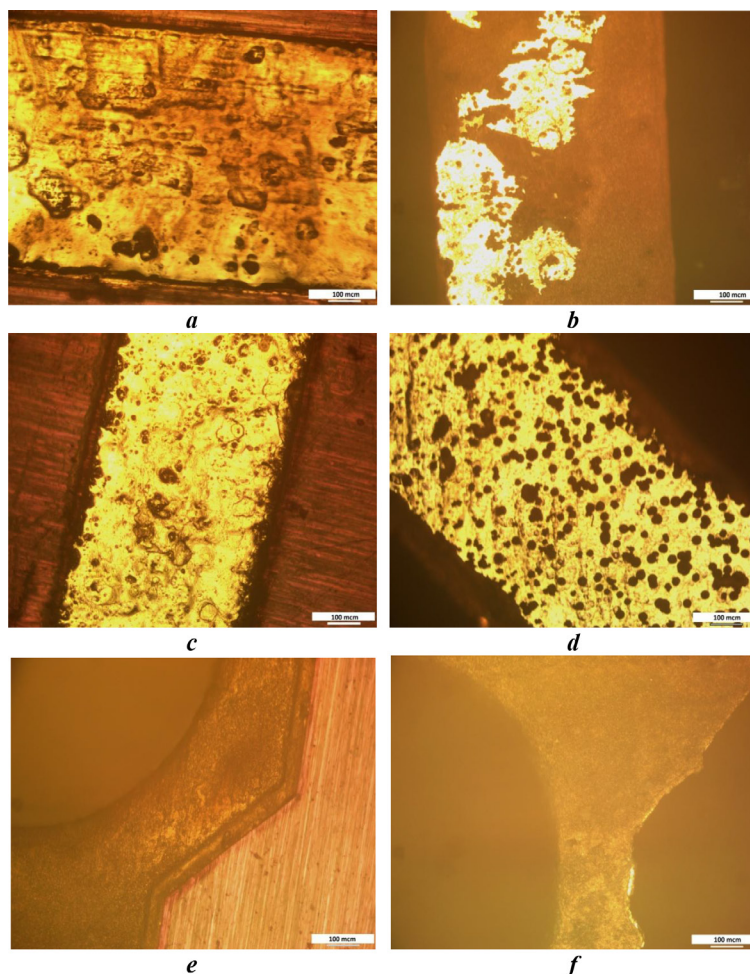


Fig. 4. Photographs of fragments of a conductive pattern with an electrodeposited nickel coating before etching in an alkaline copper chloride solution (a, c, d) and after etching (b, d, e).

The coatings were deposited from electrolytes (according to Table 1): a, b – № 1; c, d – № 2; d, e – № 3

№ 1, № 2 (Table 1), partial destruction of metal resists occurs before complete etching of copper from the blank areas of the board. When using matte nickel sulfur-free coatings from electrolyte No. 3, the corresponding resist allows recreate a high-quality conductive pattern. A more detailed result of the testing of metal-resistive properties can be seen in the photo images of the surface morphology of conductive pattern with electrodeposited resistive coatings (Fig. 4). In fact, the corresponding results are consistent with the results of the corrosion rate determination. Thus, the most stable is the metal resist from matte coating deposited from electrolyte № 3, in second place is the metal resist obtained from electrolyte № 2, and in third place – from electrolyte № 1. Taking into account the sulfur content in the coatings, it turns out that with an increase in the content of the latter in the foil from 0,074 wt.% (electrolyte № 1) to 0,24 wt.% (electrolyte № 2) the corrosion rate of the foil, on the contrary, decreases. However, the corresponding sulfur contents in the foil exceed the critical permissible value, ensuring complete disruption of the passive film on nickel.

Conclusions

During the research of corrosion resistance of galvanic nickel coatings, the following was established. The use of electrolytes with the addition of saccharin 0,5...6 g/l for the deposition of nickel metal-resist leads to the formation of deposits with a sulfur content of 0.074...0.24 wt.% and low corrosion resistance (corrosion rate in alkaline copper-chloride etching solution 20 $\mu\text{A}/\text{cm}^2$). The use of electrolytes without sulfur-containing additives allows obtaining coatings with a sulfur content of up to 0.01 wt.%. The corrosion rate of these coatings in alkaline copper-chloride etching solution is the lowest and is about 3 $\mu\text{A}/\text{cm}^2$. Thus, electrodeposition of metal-resistive nickel coatings from electrolytes that do not contain sulfurogenic gloss-forming additives is important for achieving their high corrosion resistance, in particular, in alkaline copper-chloride etching solution.

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