Solution for pre-pressing surface treatment of the conductive pattern of the inner layers of multilayer printed circuit boards

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Abstract

For a long time, a standard oxidation process (GOST 23661-79) was used to enhance adhesion between the inner layers of multilayer printed circuit boards (MPCBs). As a result of this process, an oxide layer is formed on the copper surface, which has a more developed surface, leading to enhanced adhesion due to the mechanical "bonding" of the treated surface to the prepreg, a sheet of fiberglass impregnated with a thermosetting epoxy resin. However, oxidation does not provide the required adhesion of the internal layers of state-of-the-art MPCBs (with high circuit density) since the post-treatment stages of MPCBs may involve the so-called "pink ring" effect, areas of copper without an oxide layer appear around the holes because the acid solutions used at these stages (for example, microetching prior to chemical copper plating of printed circuit board holes) dissolve the oxide layer and penetrate into the interlayer space. A production process has been developed for pre-pressing preparation of the copper surface of the conductive pattern (CP) in the internal MPCB layers using a solution containing (g/L): H_2SO_4 91, H_2O_2 14, benzotriazole 8, Cl^- 8–10 mg/L, PEG (1500) 3–7. The process makes it possible to form on a copper surface, at t 35°C and in τ=75 s, a rough adhesive organometallic layer that is not inferior to the world's best analogs in terms of corrosion resistance, friability, and roughness. It has been shown that the strength of adhesion to the prepreg surface modified in the solution that we developed is comparable to that of the analogs from the world's best manufacturers of materials for printed circuit boards. It has been found that during the treatment, a rough layer with a thickness of 2.5 μm is formed on the copper surface, and an organometallic layer with a thickness of ~250 Å is formed on the surface of the rough layer itself.

Introduction

A printed circuit board (PCB) is intended for mounting and connecting components of electronic circuits that are the "brains" of modern devices, apparatuses, machines, and other equipment used in virtually any industry [1, 2].

One of the key challenges in PCB manufacturing is to provide a high strength of adhesion between the copper CP surface, on the one hand, and the metallic and non-metallic layers produced subsequently, on the other hand [3].

To provide the required adhesion strength, a rough adhesive layer is formed on the copper surface at various stages of MPCB production, for example, before pressing the inner layers of multilayer printed circuit boards, application of a photoresist and solder mask, chemical copper plating, and prior to application of finishing coatings (for example, immersion gold plating) [4, 5].

One of the most important stages in MPCB manufacturing is the formation of an adhesive layer on the inner CP layer before pressing.

For a long time, a standard oxidation process (GOST 23661-79) was used in the production of PCBs to enhance adhesion between the inner MPCB layers. As a result of this process, an oxide layer is formed on the copper surface, which has a more developed surface, resulting in the adhesion enhancement due to the mechanical "bonding" of the treated surface to the prepreg, *i.e.*, a sheet of fiberglass impregnated with a thermosetting epoxy resin. However, oxidation does not provide the required adhesion of the internal layers of state-of-the-art MPCBs (with high circuit density) due to the so-called "pink ring" effect, that is, formation of copper areas without an oxide layer around the holes, because the acid solutions used at these stages (for example, microetching before chemical copper plating of PCB holes) dissolve the oxide layer and penetrate into the interlayer space [6]. Cavities appear inside the MPCB that extend into the hole, which can affect the reliability of the board. The pink ring effect can only be detected on the end product, which increases the percentage of defects.

Another disadvantage of the oxidation process is a low thermal stability of the oxide layers, a decrease in adhesion by 30–60%, after thermal shock upon exposure to an organosilicon liquid heated to 260°C for 10 s [7].

These drawbacks of the process for preparing the copper surface before pressing the inner MPCB layers have been eliminated in the modern technologies featuring a completely different approach to the formation of adhesive layers. Instead of oxidation, it involves micro-etching of the copper surface with formation of a rough layer ~1.5–2.5 μm thick and formation on the surface of this microrelief of a thin (200–300 Å) organometallic layer, which ensures adhesion of the layers not only by increasing the contact surface area but also through formation of chemical bonds with the prepreg molecules [8, 9].

We have developed a technology for forming an adhesive organometallic layer on the CP surface before pressing, which ensures strong adhesion of the internal layers in state-of-the-art MPCBs.

Experimental

Foil dielectric plates made of FR4, which is one of the main materials employed in the production of PCBs in the Russian Federation, were used as the samples.

Preliminary preparation of samples included chemical degreasing and activation. After the chemical degreasing stage, a 2-stage washing was carried out, first in hot and then in cold water. A rough organometallic layer was formed by surface treatment for 60–90 s in a modifying solution at a temperature of 30–40°C.

The quality of the adhesive layer thus formed was estimated using data on friability, corrosion resistance, color characteristics, integrity, roughness parameters, morphology, and strength of adhesion of the surface to the prepreg.

To estimate the corrosion resistance of the organometallic layer, a solution containing 5 wt.% sulfuric acid (94%) and 5 wt.% hydrogen peroxide (37%) was used. The solution was applied dropwise to the sample surface, after which the time (in seconds) when the coating began to dissolve (the first pink dots appeared) was recorded. After the start of a violent reaction of the solution components with the copper substrate (the appearance and release of gas bubbles from the surface), the time (in seconds) required for complete dissolution was measured, after which the arithmetic mean of the time of dissolution of the organometallic coating was calculated. This is a comparative method that does not involve obtaining the absolute values.

The color characteristics of organometallic films formed on the surface of copper foil were determined with a portable X-Rite Ci60 series spectrophotometer using the CIELAB method. According to this technique, each color is associated with three numerical values (L, a, b), which determine the location of a given color in a three-dimensional coordinate system. In this way, two colors (excluding the factor of subjectivity of color perception by the human eye) can be compared by comparing the numerical values that describe them. Since the color can indirectly indicate the quality of the resulting coatings in some cases, indicators were determined that show the deviation of the color characteristics (ΔE) of the organometallic films formed from the similar characteristics for coatings obtained using the technology of one of the world's best manufacturers.

The integrity of the organometallic coatings was estimated visually.

The roughness parameters of a machined surface were measured using a SuperView W1 3D optical profilometer, a device for subnanometer measurement of various surfaces whose operating principle is based on the light interference. Combined with a Z-direction scanning module and a 3D simulating algorithm, it scans the test sample surface in a non-contact manner and then creates a 3D image.

The morphology of the surfaces being formed was studied using a Thermo Fisher Scientific Quattro C scanning electron microscope. Images were obtained using an ETD detector in secondary electron recording mode at an accelerating voltage of 10–20 kV, a probe current of 0.1–0.4 nA, an aperture size of 20 μm, and a working distance of 6–11 mm in high vacuum. The samples being studied were photographed with magnifications of ×5000 and ×20000 using a raster image diagonal length of 25 cm on the monitor which was as the device for output of primary information.

To determine the thickness and elemental composition of the organometallic layer, samples were prepared by the focused ion beam (FIB) method using a FEI Scios dual-beam

scanning electron microscope. The film surface was preliminarily protected by sputtering a metal layer (platinum) and making a thin section (50 nm) perpendicular to the surface sample. The resulting sample (5×8 μm in size) was analyzed using an FEI Osiris transmission electron microscope.

The strength of adhesion of the treated copper foil to the prepreg was assessed in accordance with GOST 26246.0-89.

To assess quantitatively the friability of the adhesive layer formed on the copper surface, a technique was developed according to which an adhesive tape (as determined by ASTM D3359) was glued onto the samples with rolling movements (with the same force), and after 3 minutes it was torn off at an angle of 90° relative to the test sample's surface. The relative amount of the coating remaining on the adhesive tape was determined by X-Ray fluorescence spectrometry using an EDX-7000 spectrometer (Shimadzu, Japan). The friability of the layer was estimated using the formula:

$$v = \frac{I_i}{I_0}$$

where I_i is the intensity of the copper signal on the adhesive tape after separation from the test sample and I_0 is intensity of the copper signal on the adhesive tape after separation from the sample treated using the technology from one of the world's leading manufacturers.

Results and Discussion

In the production of MPCB, depending on the requirements for surface roughness, various microetching solutions are used, whose main components that provide copper etching comprise a mineral or organic acid and an oxidizing agent:

$$Cu + [O] \rightarrow CuO$$

$$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O$$
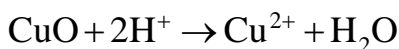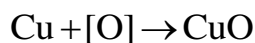
The oxidizing agents are usually persulfate ions or hydrogen peroxide [10–12].

To form an adhesive organometallic layer on the inner MPCB layers before pressing, microetching solutions are used most often. They are based on sulfuric acid and hydrogen peroxide as the oxidizing agent. The advantages of such systems compared to persulfate solutions include a high copper capacity (up to 40 g/L), lower consumption of chemicals, and stability of the etching rate [4].

To prevent excessive etching of copper, corrosion inhibitors (CIs) are added to the microetching solutions. They are compounds from the class of nitrogen-containing heterocyclic hydrocarbons, for example, benzotriazole, triazole, tetrazole, imidazole, *etc*. [13, 14]. To form a developed microrelief, it is necessary to activate the surface locally (along the grain boundaries); for this purpose, depassivators usually chloride ions, are added to the microetching solution [15, 16].

Studies have shown that of the above inhibitors, benzotriazole (BTA) is most suitable for achieving this goal, since when it is present in the solution in combination with chloride ions, a rough layer up to 2.5 microns thick can be formed. However, it should be noted that the roughness of the adhesion layer over the sample surface is not uniform. Addition of a water-soluble polymer (for example, polyethylene oxide, polyethylene glycol, polypropylene glycol, or polyvinyl alcohol with various molecular weights) to the modifying solution is known to improve the uniformity of the adhesion layer by the parameter specified above [17]. It has been proved experimentally that polyethylene glycol with a molecular weight of 1500 is the most efficient compound of those listed above.

This study aims at the development of a modifying solution for the formation of adhesive layers on the copper surface before pressing inner MPCB layers. The dependence of the adhesion layer characteristics on the concentration of the components in the modifying solution based on sulfuric acid and hydrogen peroxide, which also contains BTA, water-soluble polymer PEG 1500 and chloride ions as an inhibitor, has been studied.

Table 1 presents data on the corrosion resistance, friability of coatings, and color characteristics of the adhesion layer formed in solutions with various concentrations of hydrogen peroxide. The best results were obtained at hydrogen peroxide concentrations of 13–15 g/L. In this case, a continuous coating was formed, which was not inferior to its analog in corrosion resistance and friability, while its color characteristics deviated only slightly from those of the standard ($\Delta E = 2.5$–2.9).

The friability of the coatings obtained in solutions with hydrogen peroxide concentrations in the ranges of 7.5–11.5 g/L and 16.5–19.0 g/L is lower than that of the analog; however, this may be due to the low thickness of the adhesive rough layer formed.

Table 1. Dependence of the adhesion layer characteristics on the hydrogen peroxide concentration in the solution.

Criteria of coating quality estimation		H_2O_2 concentration, g/L									Analog
		7.5	**9.5**	**11.5**	**13.0**	**14.0**	**15.0**	**16.5**	**17.5**	**19.0**	
ΔE*		11.8	7.1	3.3	2.9	2.5	2.9	3.0	3.5	3.8	–
ν		0.57	0.78	0.86	0.96	0.86	0.99	0.45	0.3	0.14	1
CR, s	τ of dissolution beginning	3	3	4	4	4	4	3	2	2	4
	τ of complete dissolution	12	16	24	27	27	28	28	28	24	27

* deviation of color characteristics from reference values (color characteristics of analog); ν – friability; CR – corrosion resistance.

The dependence of the adhesion layer characteristics on the BTA concentration in the solution was studied. The coatings that are not inferior in corrosion resistance and friability properties to the analog are formed in the solution containing 8 g/L BTA (Table 2). A further increase in the inhibitor concentration leads to a decrease in the corrosion resistance and friability of the adhesive coating formed, which may also be due to the formation of a thinner adhesive organometallic layer.

Table 2. Dependence of the characteristics of the adhesion layer on the benzotriazole concentration in the solutions.

Criteria of coating quality estimation		Concentration of corrosion inhibitor, g/L										Analog
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	
ΔE		35.7	30.5	21.6	14.8	9.0	1.7	0.8	2.5	4.7	6.4	–
ν		0.72	1.05	1.18	2.94	2.14	1.49	1.25	0.94	0.69	0.28	1
CR, s	τ of dissolution beginning	1	1	1	2	3	3	4	4	3	3	4
	τ of complete dissolution	4	5	7	8	17	21	21	27	26	20	27

To assess the effect of BTA concentration on the roughness of the adhesion layer formed, profilograms and 3D images were obtained (Figure 1) and the roughness parameters of the surface treated in a solution with various concentrations of the inhibitor were determined (Figure 2). It can be seen that with an increase in the concentration of the corrosion inhibitor in the solution to 8 g/L, the roughness of the treated surface increases: Ra increases from 0.3 to 0.6 μm. A further increase in the inhibitor concentration to 12 g/L leads to a decrease in Ra to 0.3 μm. Apparently, if the inhibitor is present in excess, it is adsorbed not only on the crystallite faces, but also along the grain boundaries, thus hindering the metal etching in these areas.

Chloride ions are among the main components of the modifying solution. According to published data, if the content of chloride ions in the solution is low (1 to 50 mg/L), they are predominantly adsorbed along the boundaries of crystal grains and depassivate copper etching in these zones. In the opinion of certain researchers, this leads to preferential etching of copper along the indicated boundaries, which contributes to the development of a microrelief on the treated surface [17–19].
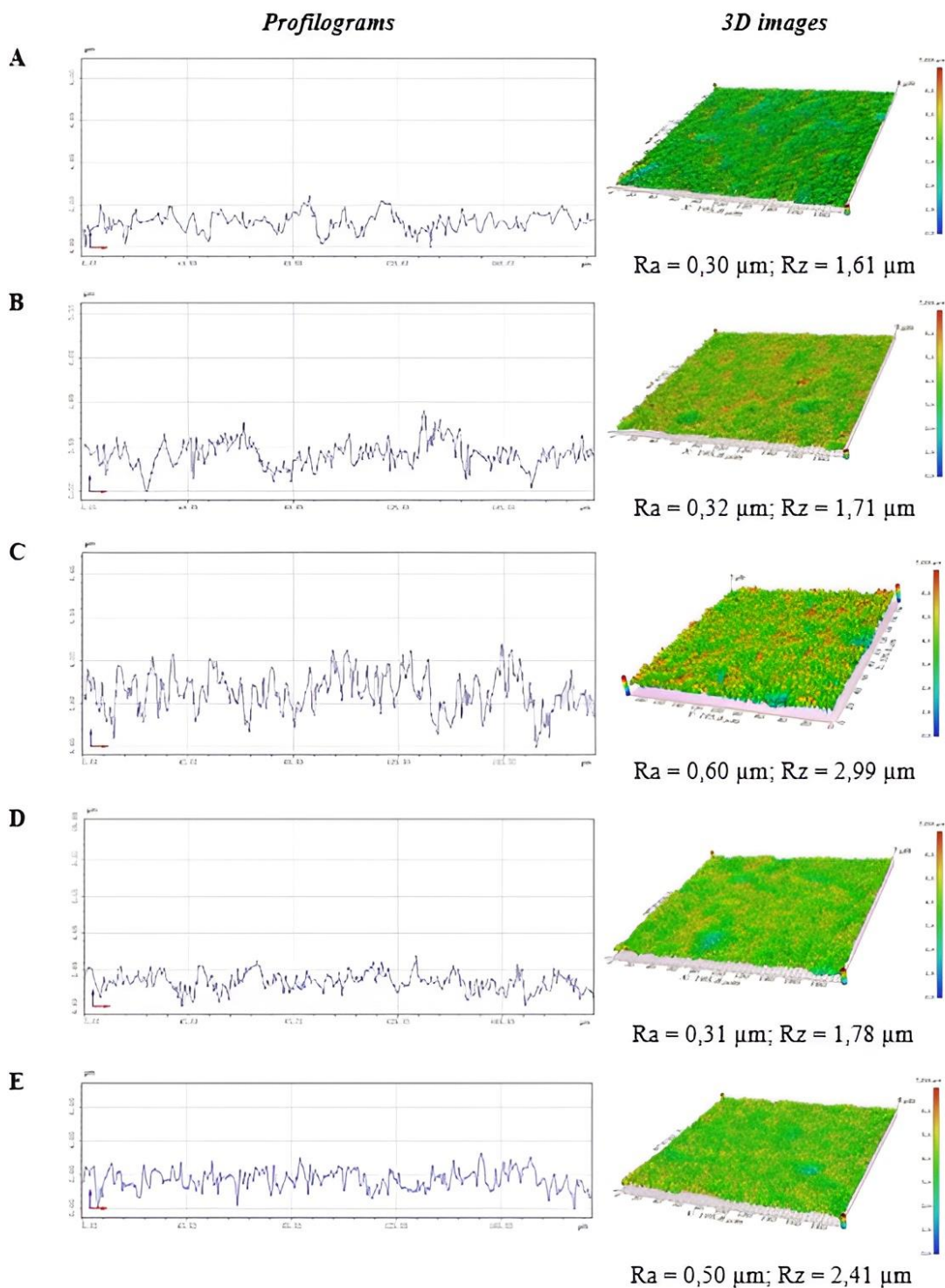
Profilograms   **3D images**

A

Ra = 0,30 μm; Rz = 1,61 μm

B

Ra = 0,32 μm; Rz = 1,71 μm

C

Ra = 0,60 μm; Rz = 2,99 μm

D

Ra = 0,31 μm; Rz = 1,78 μm

E

Ra = 0,50 μm; Rz = 2,41 μm

Figure 1. Profilograms and 3D images of the surface of samples treated in solutions containing various concentrations of the corrosion inhibitor: A – 0 g/L; B – 4 g/L; C – 8 g/L; D – 12 g/L; E – analog.
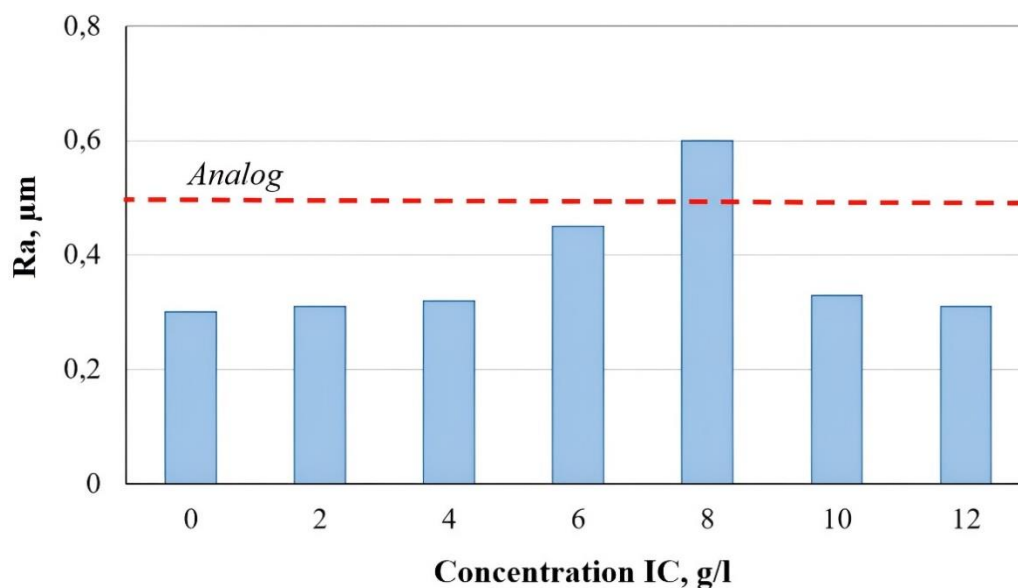
Figure 2. Dependence of surface roughness of the adhesion layer on the CI concentration.

Profilograms and 3D images of the adhesion layer surface formed in solutions with various concentrations of chloride ions, as well as the dependence of roughness parameters on the concentration of chloride ions in the solution, are presented in Figures 3 and 4. It can be seen that the roughness parameters of the samples processed in a solution containing 8–10 mg/L chloride ions are comparable to those of the analog.

The results displayed in Table 3 show that the concentration range of chloride ions acceptable for the solution in question is 8–10 mg/L. Outside this range, the adhesion layer is inferior in the corrosion and friability properties to its analogue, and along with this, the deviation of color characteristics is enhanced.

The SEM images of the surface displayed in Figure 5 indicate that the adhesion layer structure matches most closely that of the analog if the solution contains more than 8 mg/L chloride ions.

The strength of adhesion of a prepreg copper surface with an adhesion layer formed in solutions with various content of chloride ions was studied (Figure 6).

It can be seen that the adhesion of the copper surface to the prepreg is the strongest if the adhesion layer is formed in a solution containing 8 mg/L chloride ions.

Given the results obtained, we can conclude that the optimal concentration of chloride ions in the modifying solution is 8–10 mg/L.

A study of the dependence of the adhesion layer characteristics on the PEG-1500 concentration showed that the smallest deviation of color characteristics from the characteristics of the standard corresponds to a water-soluble polymer concentration of 3–7 g/L, which indirectly indicates the formation of a microrelief with uniform structure (Table 4). As regards the corrosion resistance and friability properties, the adhesion layer is not inferior to its analog, either. Decreasing the concentration of polyethylene glycol in the

solution does not have a positive effect on the uniformity of the coating formed, while increasing this concentration leads to enhanced friability of the layer.
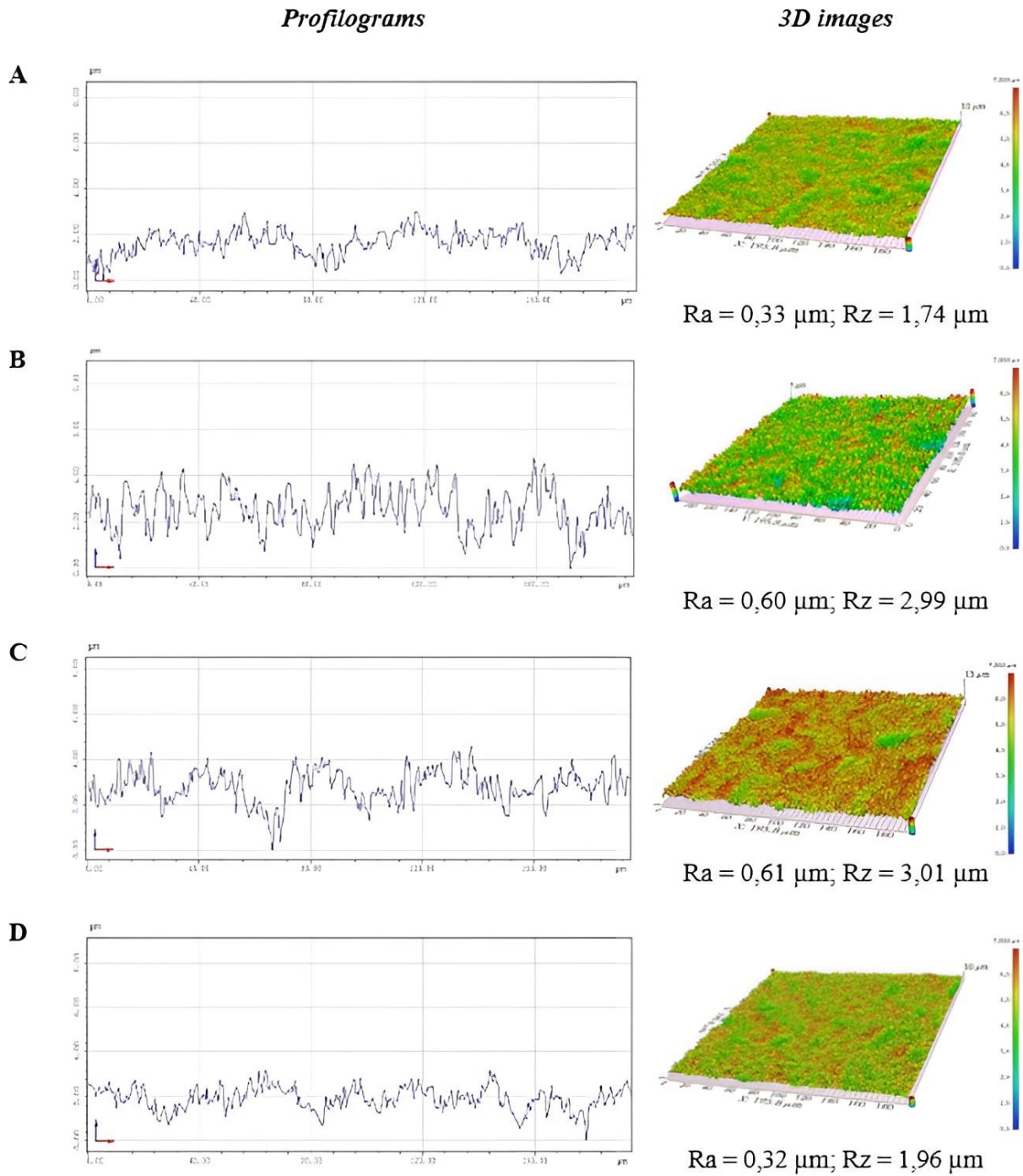

Figure 3. Profilograms and 3D images of the surface of samples treated in solutions containing various chloride ions concentrations: A – 0 mg/L; B – 8 mg/L; C – 12 mg/L; D – 20 mg/L.
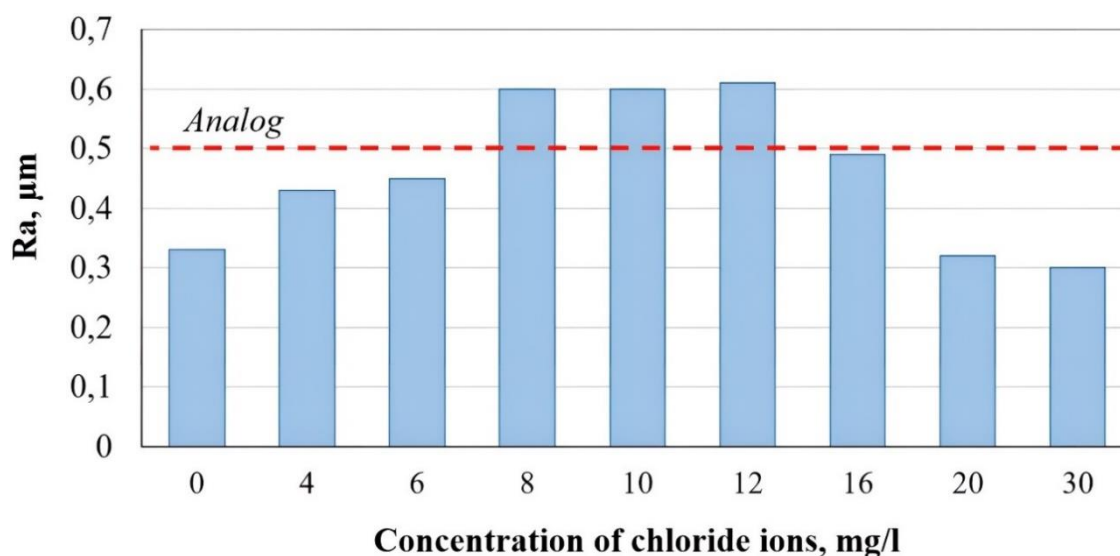
Figure 4. Dependence of surface roughness of the adhesion layer on the concentration of chloride ions.

Table 3. Dependence of the characteristics of the adhesion layer on the concentration of chloride ions in the solution.

Criteria of coating quality estimation		Cl^- concentration, mg/L								Analog
		6	**7**	**8**	**10**	**12**	**16**	**20**	**22**	
ΔE		7.7	4.5	2.5	1.0	1.6	7.0	14.3	17.9	–
ν		0.28	0.48	0.93	1.87	3.2	1.87	1.28	0.49	1
CR, s	τ of dissolution beginning	2	3	4	4	4	3	3	1	4
	τ of complete dissolution	18	23	27	27	22	18	12	9	27

Thus, adhesive layers on a copper surface that are not inferior to their analog in terms of corrosion resistance, friability, roughness parameters, and strength of adhesion to the prepreg are formed in the solution containing (g/L): H_2SO_4 91; H_2O_2 14; CI 8; Cl^- 8–10 mg/L; PEG (1500) 3–7.

It is known from the literature that the adhesion layer formed on the copper surface in state-of-the-art modifying solutions before pressing the internal MPCB layers is a 1.5–2.5 μm thick rough layer; it includes the thinnest surface organometallic layer 20–30 nm thick, which is formed due to the presence of a nitrogen-containing (for example, heterocyclic) compound in the solution [9] (Figure 7).
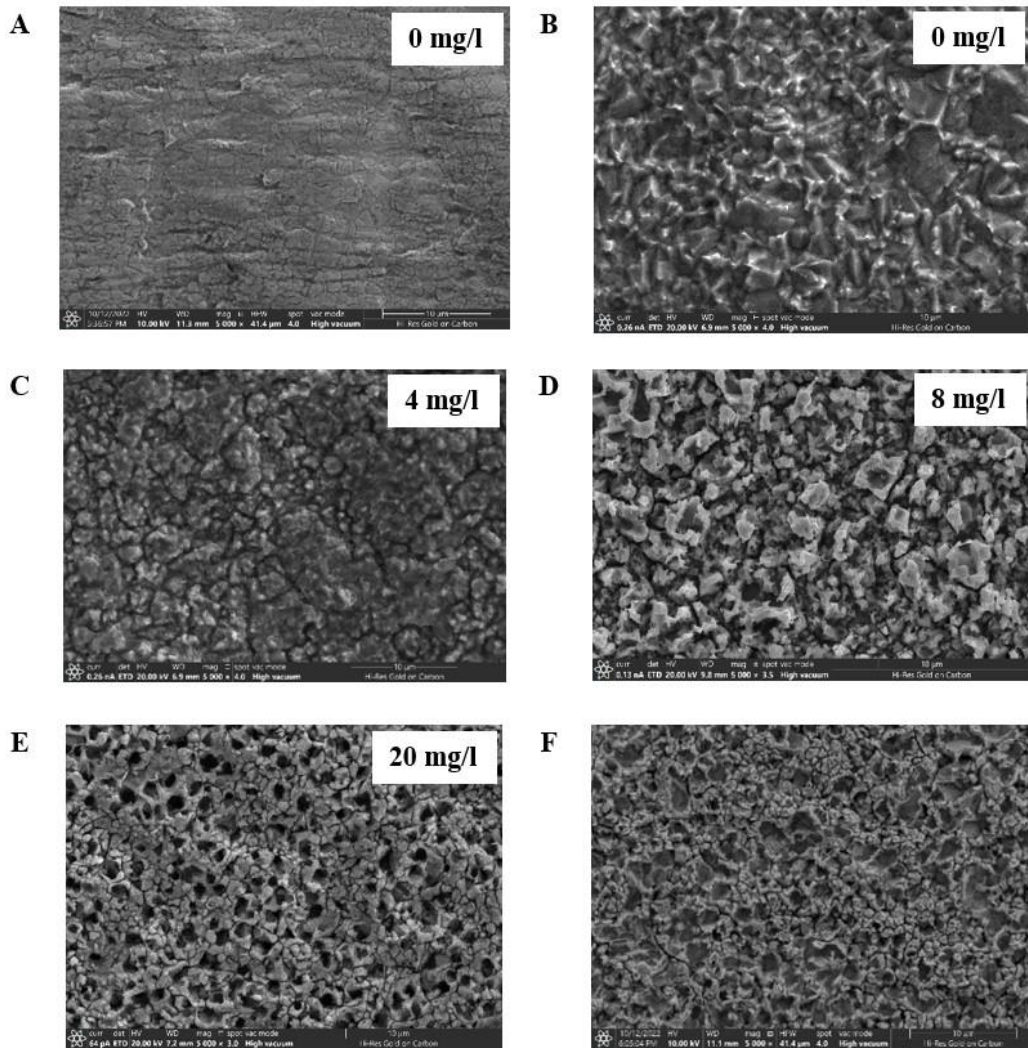
Figure 5. Photographs of the surface of samples treated in solutions containing various concentrations of chloride ions: A – untreated surface; B – 0 mg/L; C – 4 mg/L; D – 8 mg/L; E – 20 mg/L; F – analog.
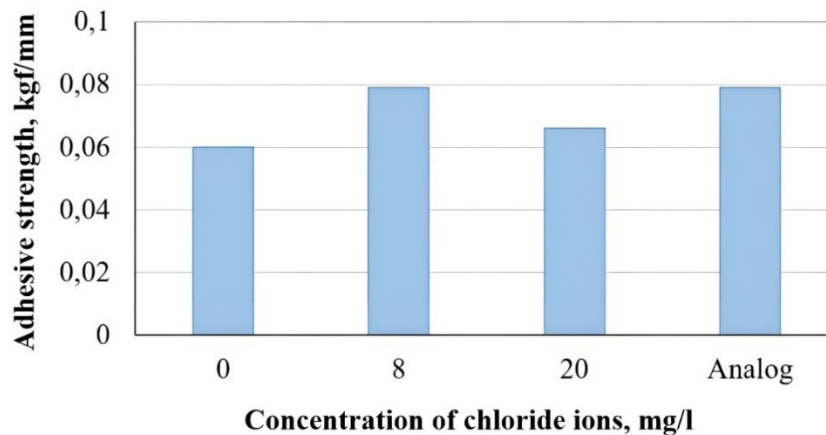

Figure 6. Dependence of strength of adhesion of copper surface to pre-preg on the concentration of chloride ions in the solution.

Table 4. Dependence of the characteristics of the adhesion layer on PEG 1500 concentration in the solution.

Criteria of coating quality estimation		PEG−1500 concentration, g/L										Analog
		1	2	3	4	5	6	7	8	9	10	
ΔE		1.8	1.5	0.7	0.7	0.5	0.4	0.4	0.4	0.9	1.0	–
v		1.49	2.40	1.05	1	1	1.02	1.04	2.07	2.24	2.13	1
CR, s	τ of dissolution beginning	4	4	4	4	4	4	4	4	4	4	4
	τ of complete dissolution	20	22	26	27	26	26	25	25	25	25	27
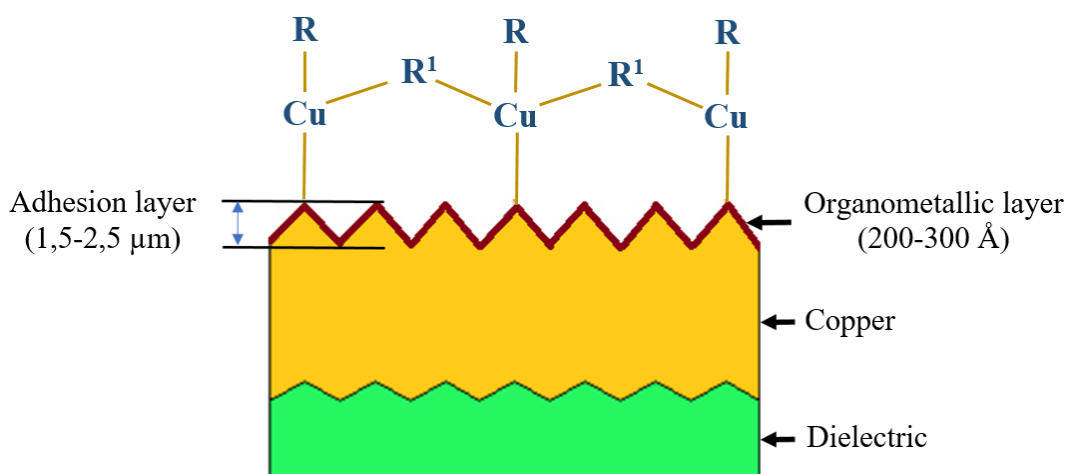
Figure 7. Structure of the organometallic adhesion layer (scheme).

To determine the thickness of the rough adhesive layer, transverse sections of samples treated in the developed solution following the technology of one of the world's best manufacturers were prepared, and images were made with a scanning electron microscope (Figure 8).

The images displayed above clearly show that the thickness of the adhesion layer formed in the developed solution (2.536 μm) is comparable to that of the analog (2.455 μm).

TEM analysis of a sample prepared by the FIB method was used to determine the thickness and elemental composition of the thinnest organometallic surface layer.

The data presented in Figure 9 indicate that the thickness of the organometallic layer (in the diagram, the nitrogen-containing region is bounded by red dotted lines) is about 25 nm (250 Å), which agrees with published data. As expected, the organometallic layer formed due to the presence of BTA in the solution contains the following elements: N, C, Cu.
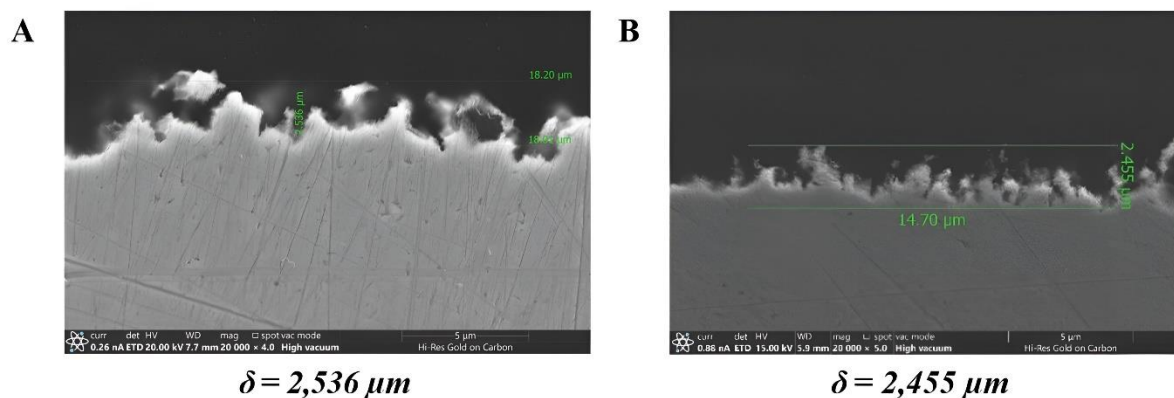
$\delta = 2{,}536\ \mu m$ $\delta = 2{,}455\ \mu m$

Figure 8. Photographs of cross sections of samples (×20000) treated with: A – the solution developed in this study; B – analog.
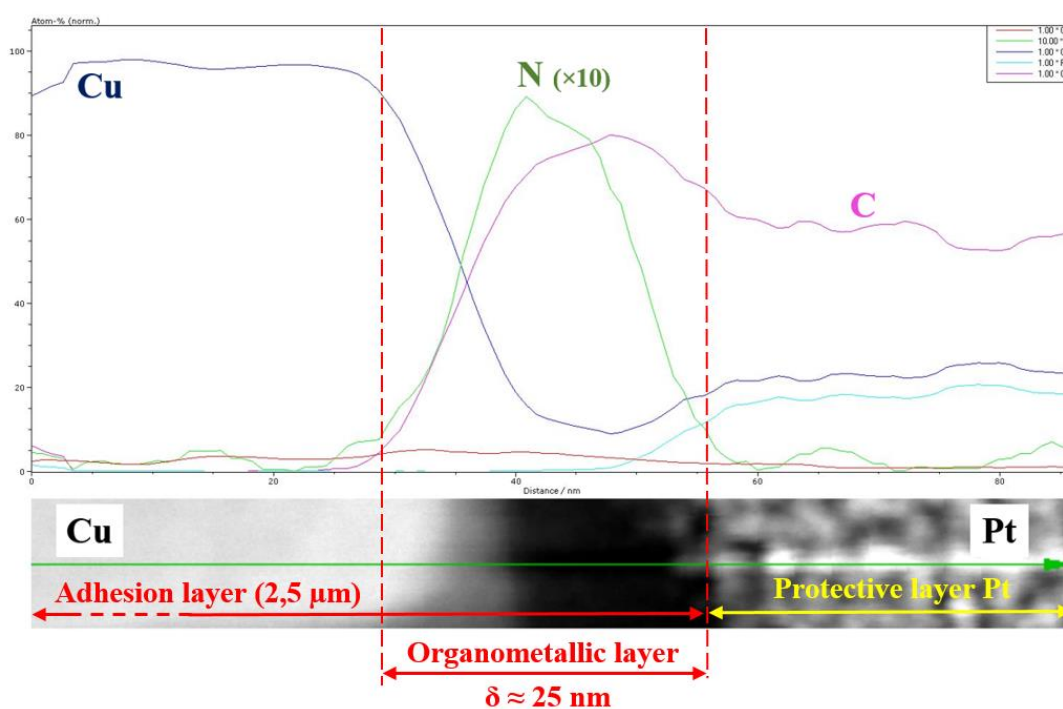

Figure 9. Distribution of elements across the thickness of the adhesion layer.

It should be noted that the structure of the adhesive layer formed in the developed solution is identical to that of its analog.

Conclusions

A solution has been developed containing (g/L): H_2SO_4 91, H_2O_2 14, BTA 8, Cl^- 8–10 mg/L, and PEG (1500) 3–7, which makes it possible to form (at $t=35°C$, $\tau=75$ s) a rough adhesive organometallic layer on copper surface that is not inferior to the world's best analogs in corrosion resistance, friability, and strength of adhesion to the prepreg.

It has been shown that the thickness of the rough adhesion layer formed is 2.54 μm, while that of the surface organometallic layer is 250 Å.

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