Study of immersion tin plating for the production of printed circuit boards

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Abstract

An immersion tin plating solution has been developed for deposition of finishing tin coatings onto the surface of the current-conducting pattern (hereinafter referred to as CCP) on printed circuit boards (hereinafter referred to as PCB). Finishing tin coatings are intended for the protection of CCP on printed circuit boards from corrosion to provide high surface wettability with solder and maintain the solderability and weldability for a long time (up to 6 months). Finishing immersion tin coatings are also designed to ensure coplanarity of the CCP surface. The solution contains (g (mL)/L): Sn^{2+} 12; CH_3SO_3H 40; $C_3H_5O(COOH)_3$ 300; PEG-400 170; $CS(NH_2)_2$ 100; $Na(H_2PO_2)$ 25; TsKN-32M 1; and Ag^+ 0.025. It enables depositing in 2 stages (at t=18–25°C and τ=2 min, then at t=70°C and τ=14 min) tin coatings the solderability of which meets the requirements and is not impaired after exposure to steam for 4 hours. It was revealed that with increasing temperature of the working solution, the thickness of the tin coating increased, while the crystal structure became coarser. Preliminary immersion tin plating in a cold solution was shown to results in a finer structure of the subsequent layer deposited in hot solution. It was found that sodium hypophosphite enhanced the stability of the solution and improved the reproducibility of the coating thickness and structure. An antioxidant was selected, TsKN-32M, which, by preventing the oxidation of tin(II) to tin(IV), enhanced the stability of the solution. It was found that no formation of whiskers in silver-doped tin coatings is observed after 3 months of aging.

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Introduction

Obtaining proper and reliable soldered joints in electronic equipment depends on many design and process factors, including the required solderability of the elements to be connected, *i.e.*, components and conductors of printed circuit boards. To maintain the solderability of CCP in printed circuit boards before installing the electronic components and to ensure the flatness (coplanarity) of the coating and reliable installation of soldered

connections, the so-called finishing coatings are applied on the copper surface of the contact pads of the CCP in a printed circuit board. These coatings, along with protecting CCP from corrosion, provide the required functional characteristics of the contact pad surface.

The protective finishing coatings for PCBs should provide high wettability of the surface with solder and preservation of solderability and weldability for a long time (up to 6 months) and the strength of soldered and welded joints during PCB operation.

Immersion tin coating feature the properties necessary for finishing coatings: high solderability (second best after HASL (Figure 1)), surface coplanarity, which is superior to that obtained by hot tinning, and a price low compared to the immersion gold plating process [1]. The use of tin immersion coating as a PCB finish coating has been limited for some time due to the propensity for whisker growth and the porosity of the coating [2]. Moreover, the liability to the formation and continuous growth of intermetallic compounds at the copper-tin interface followed by their oxidation significantly worsened the solderability of coating [3]. These shortcomings have been eliminated in the latest generation of tin immersion technologies developed outside Russia. The domestic developments in this area made in the 1980s fail to meet the modern requirements for solution stability and characteristics of coatings. Until recently, Russia-based PCB manufacturers were using imported technologies offered by Atotech, Ormecon (Germany), J-Kem (Sweden), and Alfachimici (Italy) [4]. Under the sanctions policy, this is no longer possible, and the development of a domestic tin immersion technology for PCB manufacturing has become more urgent.

This study is devoted to the development of a technology for application of immersion tin coatings to a PCB surface.

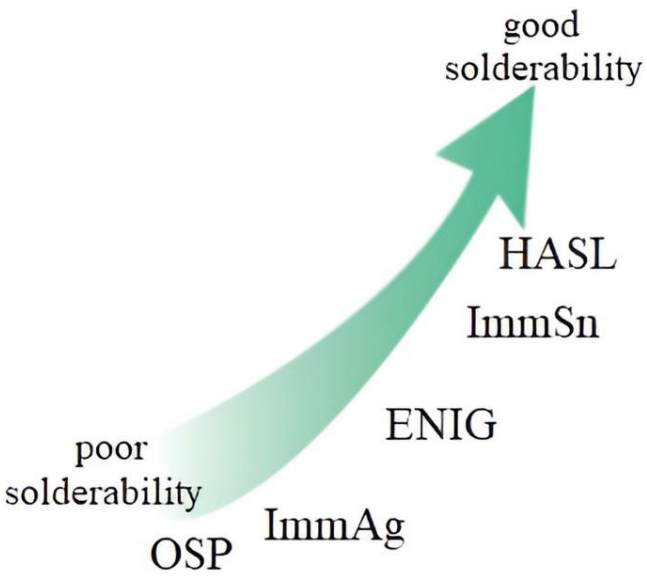

Figure 1. Solderability of finishing coatings on a PCB.

Experimental

Plates made of a foil dielectric of FR-4 grade with dimensions 2×3 cm were used as samples.

The solutions were prepared using chemical reagents of the "pure" and "analytical" grades and distilled water.

The pH of the prepared solutions was less than 1.

Prior to applying the tin coating, surface preparation was performed, which included acid cleaning (98% H_2SO_4, 40–50 mL/L; $(NH_4)_2S_2O_8$, 20 g/L; nonionic surfactant, 1–2 g/L; and cationic surfactant, 0.4–0.6 g/L) and microetching (Micro-etch 7227 S, 60 g/L; 98% H_2SO_4, 7 mL/L; and Cu^{2+}, 4 g/L).

The elemental composition and thickness of the coating were examined by X-ray fluorescence spectrometry using an EDX-7000 energy dispersive spectrometer (Shimadzu, Japan).

The content of tin(II) and copper(II) ions in the solution was determined by complexometric titration methods. To determine the tin(II) content in the solution, the methyl-thymol blue indicator was used, and a PAN indicator was applied to determine copper(II) ions.

The roughness parameters of the treated surface were measured using a SuperView W1 3D optical profilometer. Combined with a Z-direction scanning module and a 3D simulating algorithm, it scans the surface of a test sample in non-contact mode to create a 3D image.

The surface structure of the samples was studied using a Thermo Fisher Scientific Quattro C scanning electron microscope: the samples were scanned with a focused electron beam and the signal resulting from the interaction of the electron beam with the sample was recorded by a detector.

Solderability was tested in accordance with GOST 28211-89 [5].

Results and Discussion

The immersion deposition process involves the transfer of electrons from a more negative metal to a more positive metal according to reaction (1) to form a tin coating on the copper surface.

$$Cu^0 + Sn^{2+} \rightarrow Cu^{2+} + Sn^0 \quad (1)$$

The difference between the standard electrode potentials of copper and tin is approximately 0.5 V. Given this fact, to shift the potential of copper to negative values relative to tin and enable immersion tin plating, a compound should be selected as a ligand that forms stronger complexes with copper than with tin. Based on the stability constants of complexes, we chose thiocarbamide that forms a strong complex with copper ions ($K_{stab}\cdot 10^{15.4}$) and a very unstable complex with tin(II) ions ($K_{stab}\cdot 10^{1.3}$) [6].

Taking into account the published data and our preliminary experiments, a solution with the following composition (g/L) was prepared for further studies: Sn^{2+} 10–14; CH_3SO_3H 30–50; $C_3H_5O(COOH)_3$ 300; PEG-400 170; $CS(NH_2)_2$ 80–100.

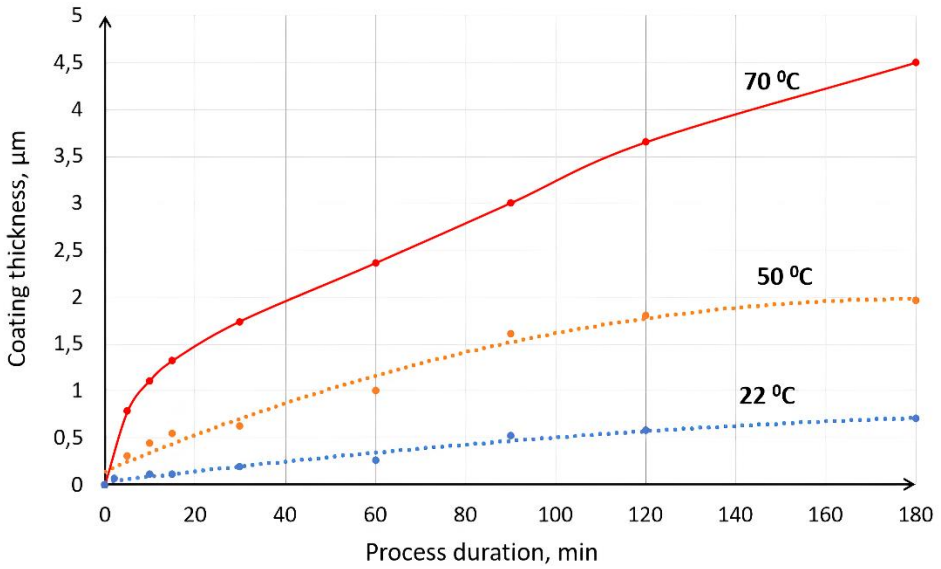

Figure 2. Tin coating thickness as a function of process duration at various temperatures.

Tin was added to the solution as tin methanesulfonate based on the higher solubility of this salt compared to tin sulfate. Citric acid was added to prevent the formation of metatinic acid [7]. Preparing the solution required enhancing the solubility of thiocarbamide; for this purpose, PEG-400 was added to the solution.

The known foreign solutions for immersion tin plating are efficient in the temperature range from 10 to 80°C, while the process duration is 10 to 25 minutes [8].

Figure 2 shows the tin coating thickness as a function of the process duration at various temperatures. It can be seen that the coating thickness increases the faster, the higher the temperature. The optimal thickness for the finishing tin coating is considered to be approximately 1 µm since the required solderability is achieved even at this thickness [9]. At a temperature of 70°C, a coating with an optimal thickness (1–1.2 µm) is formed in the solution in 15 minutes; at 60°C, in 30 minutes; and at 50°C, in 60 minutes. It is known that the duration of the immersion tin plating in foreign technologies is 16 minutes, and this value is regulated in the technological maps of many Russian industries. Taking into account these data and the requirements for the thickness of the immersion tin coating, a temperature of 70°C was chosen as the working temperature for further studies.

To determine the effect of temperature on the structure of the coatings, SEM images of the surface of tin coatings formed over the same period of time at various solution temperatures were obtained. To make these differences more pronounced, the process duration was chosen to be rather long (180 min). The images displayed in Figure 3 indicate that the coating obtained at 22°C features a fine-crystalline structure, while with an increase in the solution temperature to 50°C or 70°C, the structure of the coatings becomes coarser. As it can be se 0en from the above data, the dense and smooth structure of the tin coating that is required for a finishing coating is formed at solution temperatures of 18–25°C. However, the process is very slow at this temperature, and the required coating thickness is not obtained within a technologically acceptable time.

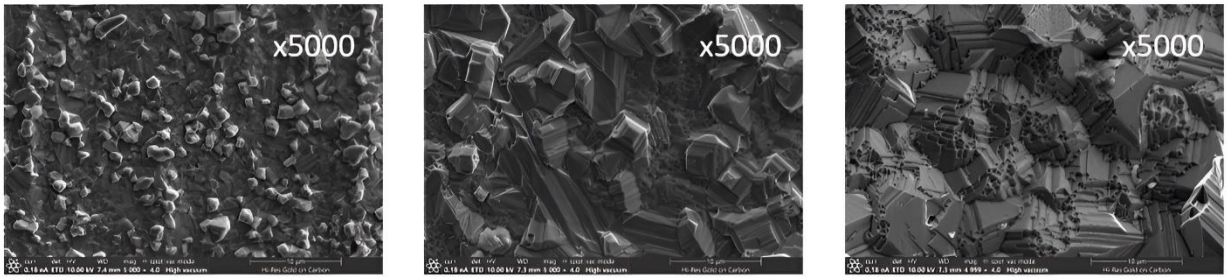

Figure 3. SEM images of tin coatings.

Given the theory and practice of deposition of metal coatings that show that up to a coating thickness of 5 μm the coating structure is largely determined by the base structure, while the thickness of the developed coatings is only 1–1.2 μm, we examined the possibility of depositing a fine-crystalline coating (within an acceptable time) by means of a two-stage process. Similar approaches were reported in some studies [10–12]. We deposited the first coating layers, which will provide the fine-crystalline structure of the subsequent layers, in a cold solution (18–25°C), and then increased the solution temperature (up to 50 and 70°C) to increase the process rate.

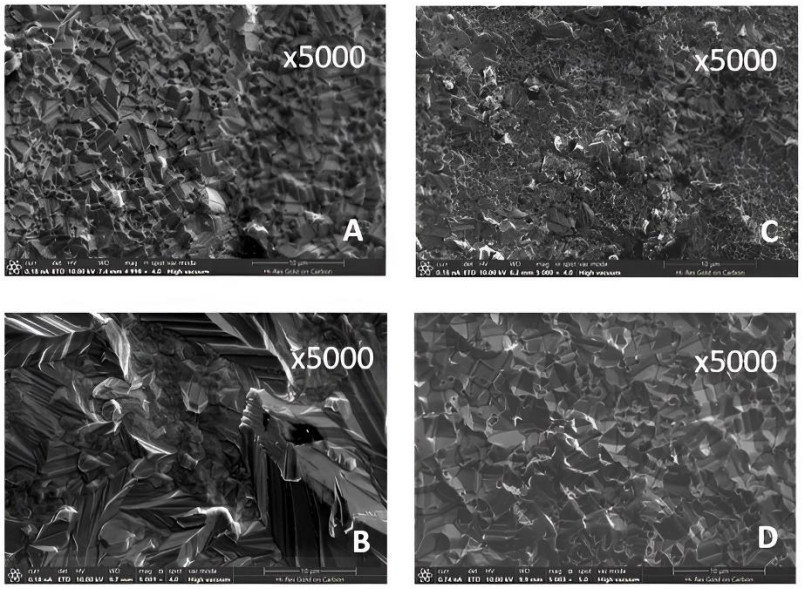

Figure 4. SEM images of the tin coatings deposited in one stage: A. t 50°C, τ 14 min; B. t 70°C, τ 14 min; two stages: C. stage I t 22°C, τ 2 min; stage II t 50°C, τ 14 min; D. stage I t 22°C, τ 2 min; stage II t 70°C, τ 14 min.

As it can be seen from the SEM images of tin coatings obtained by deposition in one (A and B) and two stages (C and D) displayed in Figure 4, preliminary tin coating for 2 minutes in the cold solution actually results in refinement of the coating structure (Figure 4). The total duration of the process for two-stage formation, similarly to the foreign analogues, is 16 minutes. Further studies were carried out using the two-stage technology.

It is reported in publications that in some cases, sodium hypophosphite is used as one of the components of immersion tin solutions [13, 14]. To estimate the role of this additive, its effect on the coating thickness was examined.

Table 1. Dependence of the tin coating thickness on the concentration of sodium hypophosphite in solution.

#	$Na(H_2PO_2)$ concentration, g/L	Coating thickness, μm		
		Experiment No.		
		1	**2**	**3**
1	0	1.25	0.92	1.47
2	25	1.2	1.2	1.22
3	50	1.58	1.56	1.57

It was found in experiments on deposition of coatings that it is not possible to obtain a coating with reproducible thickness and structure in solutions containing no sodium hypophosphite (Table 1, item 1; Figures 5A and B), while in the presence of this compound (25 or 50 g/L), the results are reproducible (Table 1, items 2 and 3; Figures 5C and D; 5E and F). Most likely, the irreproducibility of the results is due to the difference in the initial state of the copper substrate before application of the finishing coating, while in the presence of sodium hypophosphite in the solution, the copper surface is activated, which is confirmed by the values of the currentless potentials of copper given in Table 2.

The data presented in Table 1 clearly show that coatings with the required thickness are deposited in a solution containing 25 g/L of sodium hypophosphite.

With an increase in the sodium hypophosphite concentration to 50 g/L, the thickness of the coating increases by approximately 30% (Table 1, item 3). Moreover, X-ray fluorescence spectrometry and scanning electron microscopy showed that, first, phosphorus is not included in the coating deposited in a solution containing sodium hypophosphite, and, second, no tin coating is deposited on the surface of a non-foiled dielectric activated in a palladium activation solution. Therefore, the increase in the tin coating thickness is not associated with the direct reduction of Sn^{2+} by sodium hypophosphite.

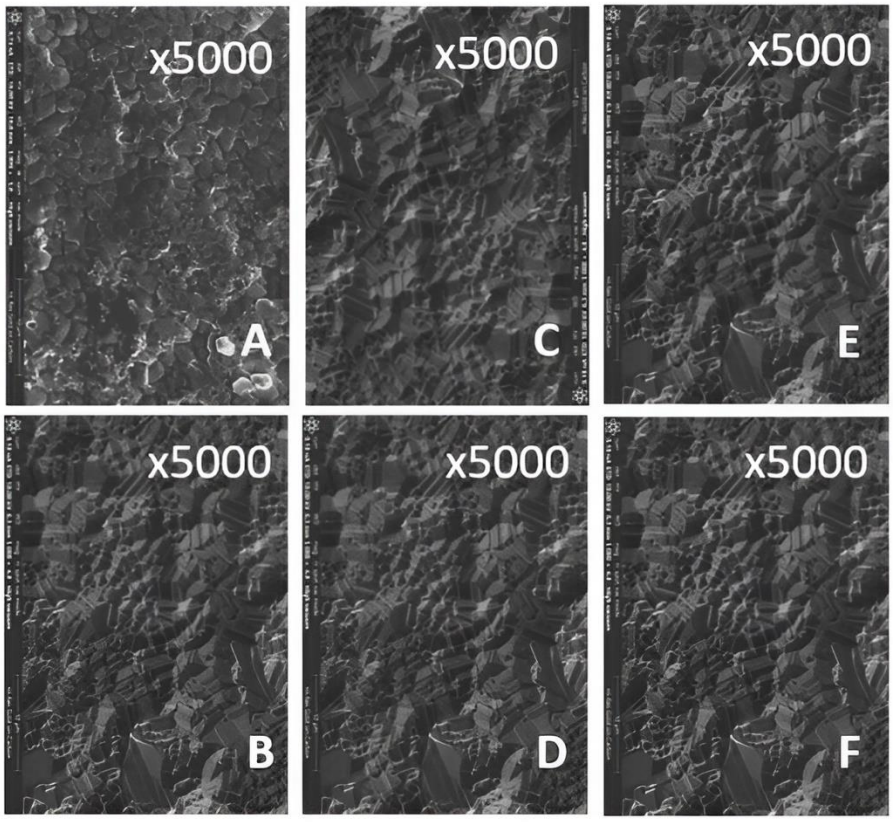

Figure 5. SEM images of tin coatings. Concentration of sodium hypophosphite in the solution: A, B. 0 g/L; C, D. 25 g/L; E, F. 50 g/L

Table 2. Currentless potentials of copper.

$Na(H_2PO_2)$ concentration, g/L	**$E_{i=0}$ (SHE), V**
0	0.518
25	0.595

Taking the results obtained into account, sodium hypophosphite was included in the solution in an amount of 25±3 g/L.

The instability of tin solutions is known to be associated with the oxidation of tin(II) by dissolved air oxygen. Antioxidants are added to solutions to suppress this process [15]. In this study we examined antioxidants such as 4-methoxyphenol and commercially available formulations TsKN-32 and TsKN-32M, the main components of which are aromatic alcohols described in publications as antioxidants of tin(II) ions [16]. The efficiency of these antioxidants was determined from the decrease in the concentration of Sn(II) in solution.

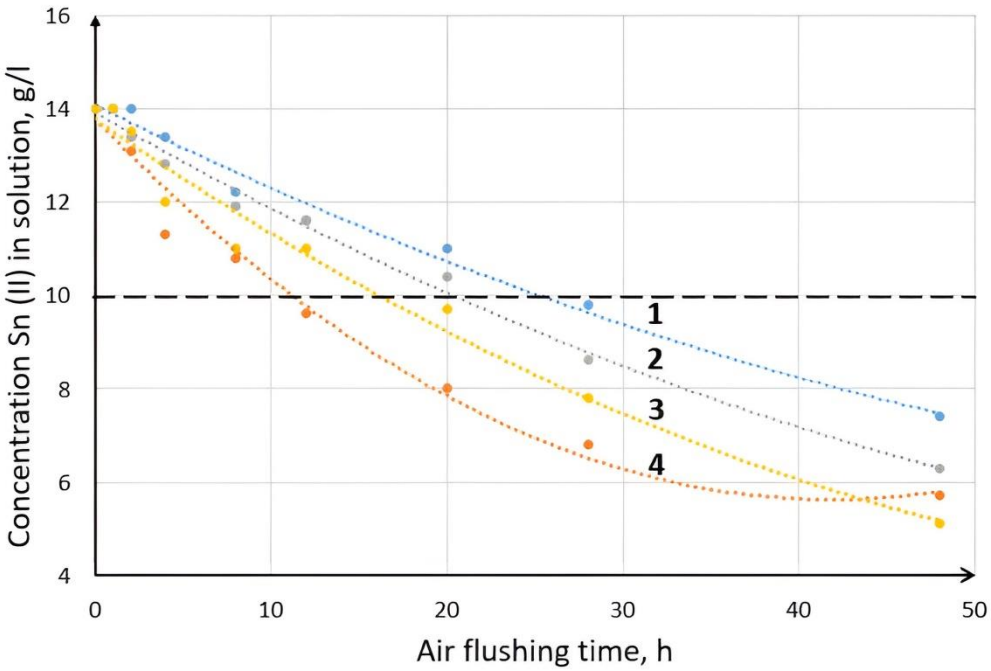

Figure 6. Change in the concentration of Sn(II) in tin solutions with various antioxidants during aging under air flushing conditions. 1. TsKN-32M (1 g/L); 2. 4-methoxyphenol (0.32 g/L); 3. TsKN-32 (5 g/L); 4. without antioxidants.

Based on the results displayed in Figure 6, the TsKN-32M formulation was chosen as the antioxidant. As it can be seen from the figure, this formulation increases the solution stability nearly twofold. This composition turned out to be more efficient compared to TsKN-32 and 4-methoxyphenol, which is used in the foreign technologies [8]. In the presence of TsKN-32M in the solution, the minimum working concentration of Sn(II) in the solution (10 g/L) is achieved after 25 hours of air flushing, while in a solution with TsKN-32, after 17 hours, and in a solution without an antioxidant it is already attained after 11 hours of flushing. In a solution with 4-methoxyphenol, the minimum working concentration of Sn(II) in the solution was achieved after 20 hours of air flushing.

The concentrations of the studied antioxidants were selected based on the manufacturers' recommendations.

The propensity of tin coatings to form whiskers is known to be a serious hazard of short-circuiting of adjacent CCP elements on a printed circuit board [17]. To inhibit whisker formation, tin is doped with metals such as antimony or silver. Silver and antimony ions were added to the solution in the form of complex compounds to shift the potential of silver and antimony to more negative values with respect to tin. We chose potassium antimonyl tartrate as a ligand for antimony ions, and for silver ions, a water-soluble sulfur-containing organic compound belonging to the class of polymer thiols; this compound was produced using the technology we developed. Its scheme is presented in Figure 7.

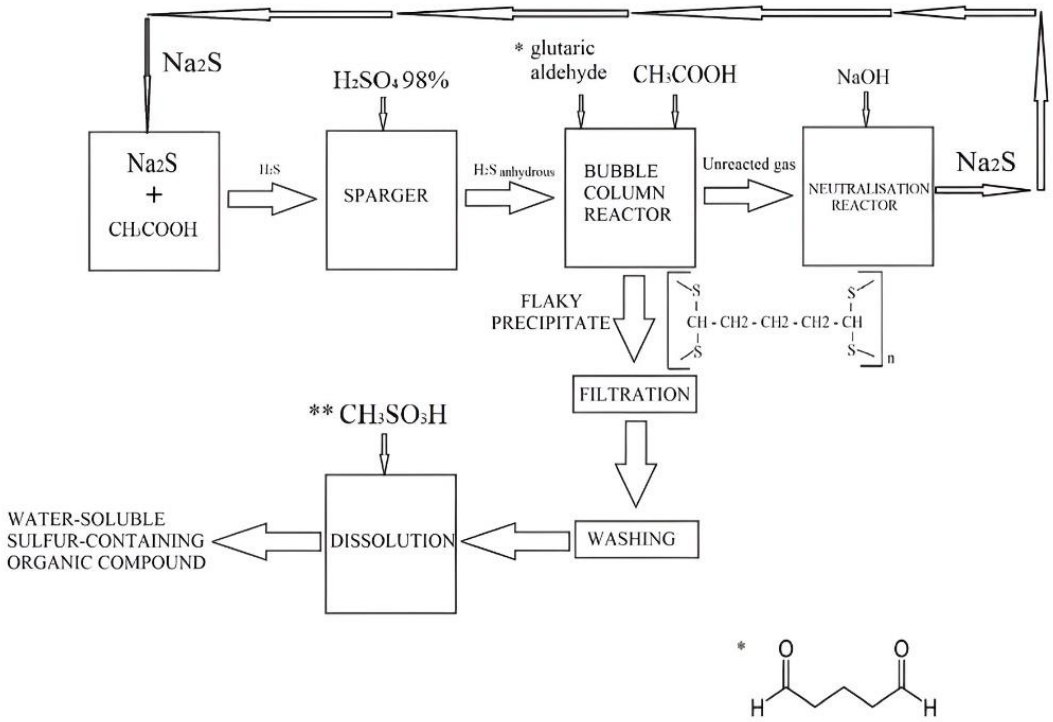

Figure 7. Scheme of preparing the ligand for silver ions.

According to the scheme shown above, hydrogen sulfide (H_2S) is formed in a Bunsen flask with a separating funnel by the reaction of sodium sulfide (Na_2S) with acetic acid (CH_3COOH). Hydrogen sulfide is supplied through a tube into a bubbler, where it is purified from moisture with concentrated sulfuric acid (H_2SO_4 98%). The H_2S purified from moisture enters the bubbler reactor with a 50% solution of glutaraldehyde acidified with acetic acid (50 mL/L). The remaining gas enters the neutralizing reactor and reacts with sodium hydroxide (NaOH) to form sodium sulfide, which is returned to the system without heating it. The end of the reaction is determined by the formation of a precipitate consisting of white polymer flakes. Then the resulting product is filtered off, washed with distilled water and an acetic acid solution, and emulsified in a solution of methanesulfonic acid.

The images of the sample surface displayed in Figure 8 show that when silver ions are added to the working solution, the appearance of the coating does not change, while addition of antimony ions worsens its appearance.

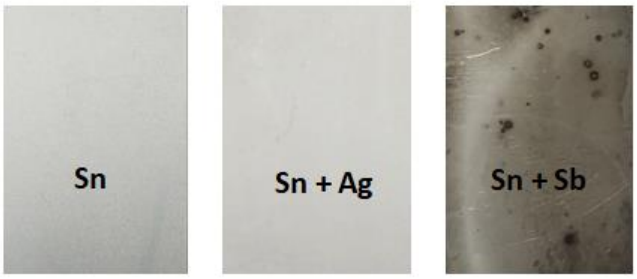

Figure 8. Appearance of tin coatings.

The SEM images of the surface of the coatings (Figure 9) show that the crystalline structure of the coatings is refined when silver or antimony ions are added to the solution, and to a greater extent in the case of antimony.

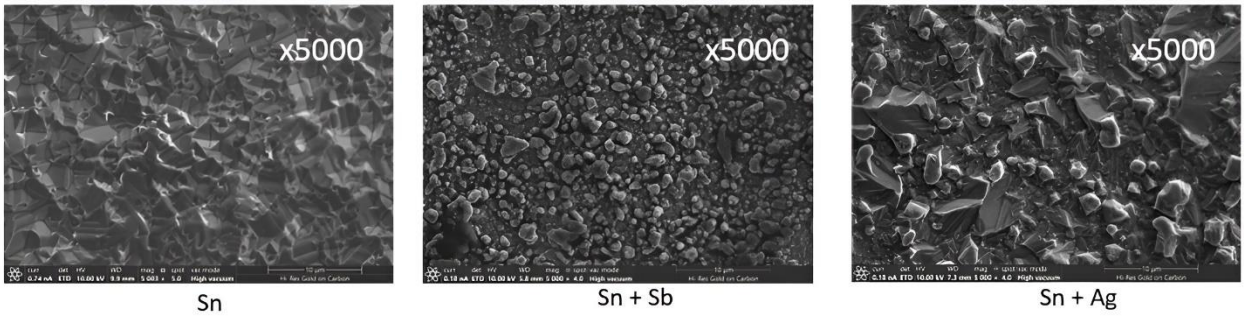

Figure 9. SEM images of tin coatings.

Taking the results obtained into account, we chose silver ions as the alloying additive that inhibits the formation of whiskers.

The data displayed in Table 3 show that the alloying additives have virtually no effect on the thickness of the resulting coatings. The content of antimony or silver in the coatings is 1–1.5%. This amount makes it possible to inhibit the growth of whiskers considerably (Figure 11).

Table 3. Composition and thickness of tin coatings.

Coatings	Thickness, μm	Content of Sb or Ag in the coating, %
Sn	1.2	0.0
Sn+Sb (0.025 g/L)	1.15	1.3
Sn+Ag (0.025 g/L)	1.15	1.3

Figures 10 and 11 present the 3D images of the surface of silver-doped and non-doped tin coatings. It can be seen that the tin coatings without alloying additives form whiskers that increase in size with time, which is a negative factor due to the risk of short-circuiting of the adjacent CCP elements on the printed circuit board. To avoid the risk of short circuiting, the whisker length should not exceed 5 μm [18]. It was found that the formation of whiskers on the surface of the developed tin coatings occurred after 2 to 3 days of aging and their length was 6 to 7 μm, which exceeds the permissible values.

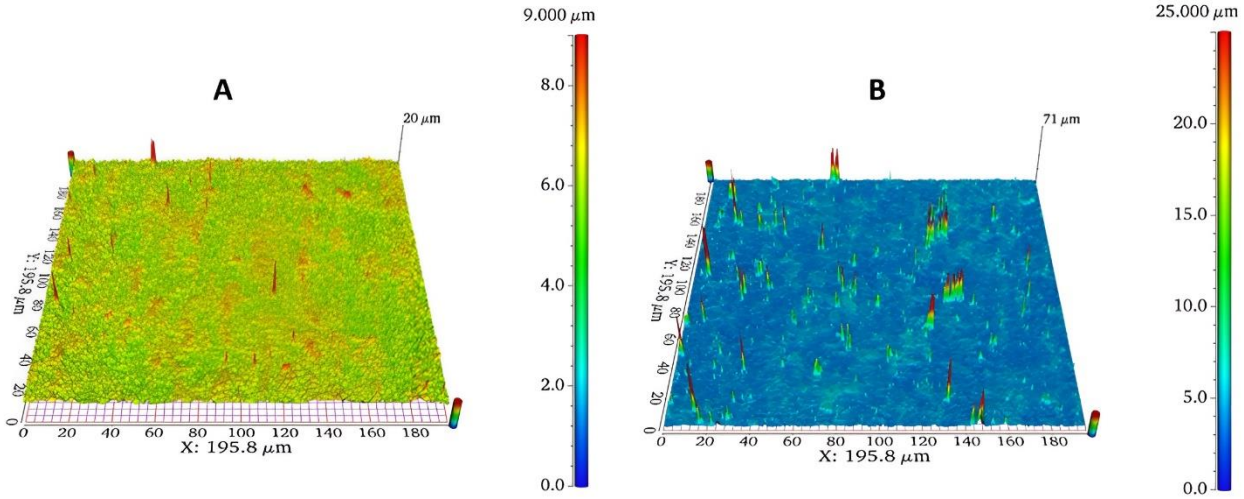

Figure 10. 3D images of the surface of tin coatings: A, 3 days of aging, $\delta_{whisker}$ 6.5 μm; B, 90 days of aging; $\delta_{whisker}$ 32 μm.

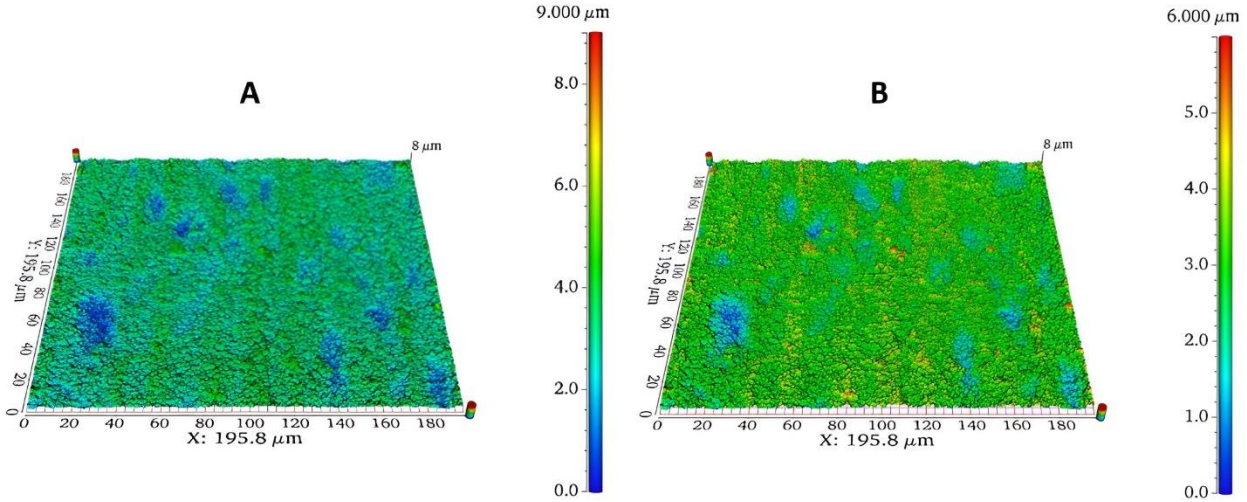

Figure 11. 3D images of the surface of silver-doped tin coatings: A, 3 days of aging; B, 90 days of aging.

It was found that in silver-doped tin coatings, whisker formation was not observed even after 3 months of aging.

In the course of immersion tin plating of copper CCP, copper ions accumulate in the solution. Figure 12 shows the thickness of tin coatings as a function of the concentration of copper ions in the working solution. It was found that when 5 g/L of copper ions accumulate in a solution, the thickness of the coating begins to gradually decrease and ceases to meet the requirements (0.8–1.2 μm) as the concentration of copper ions reaches 8 g/L. When this concentration is attained, the solution should be purified from copper ions and the content of the main components should be adjusted. The resource of this solution is similar to that of a foreign analogue [8].

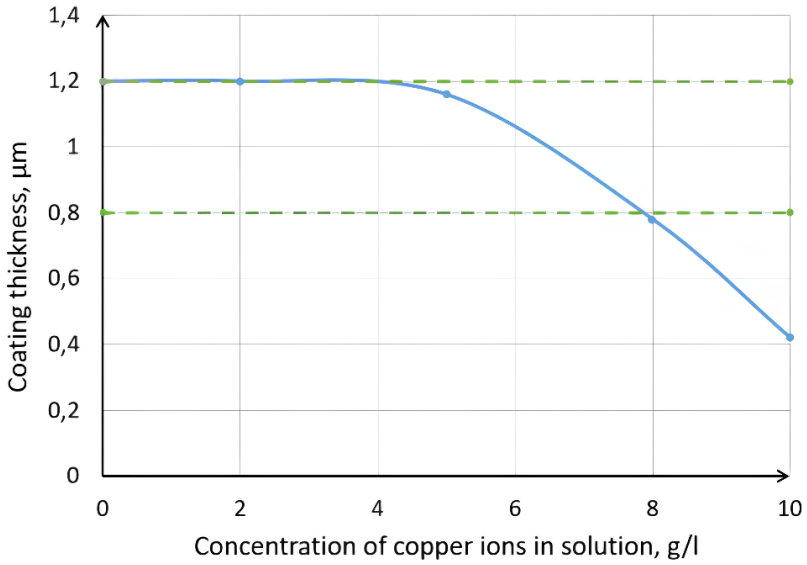

Figure 12. Tin coating thickness *vs.* concentration of copper ions in solution.

Taking the results obtained into account, the optimal composition of the solution and parameters of the technological process for deposition of immersion tin coatings were determined (Table 4):

Table 4. Optimal composition of the solution and production process parameters.

Component (parameter)	**Concentration, g (mL)/L**	
Sn^{2+}	12±2	
Methanesulfonic acid – CH_3SO_3H	40±10	
Citric acid – $C_3H_5O(COOH)_3$	300±50	
PEG-400	170±50	
Thiocarbamide – $CS(NH_2)_2$	100±20	
Sodium hypophosphite – $Na(H_2PO_2)$	25±3	
TsKN-32M	1±0.5	
Ag^+ (as a complex compound)	0.025±0.005	
Cu^{2+}	≤8	
t, °C	1. 18–25	2. 70
τ, min	1. 2	2. 14
pH	<1 (adjustment not required)	

Solderability tests have shown that immersion tin coatings deposited in the developed solution meet the requirements of GOST 28211-89, and their solderability does not deteriorate after exposure to steam for 4 hours.

Conclusions

1. A solution has been developed containing Sn^{2+} 12 g/L; CH_3SO_3H 40 mL/L; $C_3H_5O(COOH)_3$ 300 g/L; PEG-400 170 g/L; $CS(NH_2)_2$ 100 g/L; $Na(H_2PO_2)$ 25 g/L; TsKN-32M 1 g/L; and Ag^+ 0.025 g/L, which makes it possible to deposit immersion tin coatings with a thickness of 1.0–1.2 μm on a copper surface at pH<1 in two stages: at t=18–25°C and τ=2 min, and next at t=70°C and τ=14 min. The stability and service life of the solution and the functional characteristics of the deposited coatings are not inferior to those of foreign analogues.
2. It has been revealed that with increasing temperature of the working solution, the tin coating thickness increases and the crystal structure becomes coarser.
3. It has been shown that preliminary immersion tin plating in a cold solution leads to a refinement of the structure of the subsequent layer deposited in a hot solution.
4. It has been determined that sodium hypophosphite increases the stability of the solution and ensures reproducibility of the thickness and structure of the coatings.
5. An antioxidant has been selected, TsKN-32M, which enhances the stability of the solution by preventing the oxidation of tin(II) to tin(IV).
6. It has been found that whisker formation is not observed in silver-doped tin coatings after 3 months of aging.

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