Metal plating based on copper (II) complex compounds with hydroxyethylidene diphosphonic acid

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Abstract. The materials used in mechanical engineering must ensure proper work of the details and meet the requirements of the minimum complexity of its manufacture and efficiency. In this regard, the issues of improving the technological processes of obtaining metal coatings are of particular importance. This paper studies the possibility of using copper (II) complexes with hydroxyethylidene diphosphonic acid to obtain high-quality copper coatings by the method of electron paramagnetic resonance. The author determines stability constants of the complexes and their regions of existence. Moreover, the article investigates the effect of stabilizing additives on the technological characteristics of solutions of chemical copper plating. Due to the obtained results, the author developed a highly stable solution of chemical copper plating based on copper (II) complex compounds with hydroxyethylidene diphosphonic acid.

1. Introduction

A promising direction for the development of mechanical engineering, including the transport system, is the improvement of technological processes of applying metal layers on the surface of products. In recent decades, the chemical method of coating has become popular, in particular, for the metallization of dielectrics. Metallized plastics have wear resistance, chemical resistance, heat resistance and mechanical strength, have a decorative appearance and are resistant to light. Due to these properties, metallized plastic is widely used in mechanical engineering.

One of the important issues of obtaining metal coatings is the choice of complexing agents for the preparation of technological solutions. At present, a large number of complex compounds for the deposition of metals have been developed and introduced into production [1-3]. However, the search for new, more efficient ligands, which help to obtain coatings with given functional properties, is an urgent task and constantly attracts the attention of researchers.

To optimize and develop promising technological processes for obtaining metal coatings, experimental studies of the complex formation processes are necessary. From this point of view, it is of considerable theoretical and practical interest to study the patterns of complexation of complex copper (II) ions with hydroxyethylidene diphosphonic (HEDP) acid.

The choice of copper (II) hydroxyethylidene diphosphonic acid as a ligand can be explained, on the one hand, by its high complexing properties. HEDP is a polybasic acid that can serve as a complexone
in a wide pH range. The compound is non-toxic and is available on an industrial scale. One of the objectives of the study was to discover the possibility of using HEDP as ligands of copper (II) ions in chemical copper plating solutions, since the solutions of chemical copper plating currently used in practice have insufficient stability, and the complexing agent plays an important role in providing the required stability of the solutions. In connection with the problem of low-waste production, increasing the stability of chemical copper plating solutions and developing new efficient technological processes is an urgent task.

2. Methods

To research the complexation processes in the studied systems, we used the electron paramagnetic resonance (EPR) method, which is one of the most sensitive to changes in the structure and composition of the first coordination sphere of the complexing metal. The fundamentals of the EPR method and its application for the study of complex formation reactions and the state of paramagnetic ions in solutions are described in a number of papers [4–7].

The main parameters of the EPR spectra are the intensity and width of the lines, the g-factor and the constant of the hyperfine interaction, which depend on the symmetry of the nearest environment of the central ion and on the nature of the ligand.

This paper, based on the analysis and processing of the parameters of the EPR spectra of liquid and frozen solutions, explores the probable structure of the resulting complex ions, and calculates the equilibrium constants of complex formation. The EPR spectra were recorded on an RE-1306 spectrometer equipped with a magnetic field calibrator collected on the basis of a magnetic induction meter III-I-I. The samples were placed in calibrated capillaries of glass, which do not give an EPR signal in the working region of magnetic fields. The EPR spectra were recorded at 298 and 77 K in the three-centimeter wavelength range. Measurement of the g-factor of the studied complexes was carried out by comparison with the g-factor of DPPH.

The determination of the density of the unpaired electron on the central atom was carried out according to the formula:

\[ \alpha^2 = \frac{A_\parallel}{P} + \frac{3}{2} (g_\perp - 2.0023) + \frac{3}{2} (g_\parallel - 2.0023) + 0.04, \]

where \( P \) - constant characterizing the hyperfine interaction in a free uncomplexed central atom. The values \( g_\parallel, g_\perp, A_\parallel \) and \( A_\perp \) determined from spectra taken at liquid nitrogen temperature. The calculation of the equilibrium constants of complexation was carried out using the software CPRESSP (Chemical Parameters of Equilibria in Solutions with Solid Phases) [8].

We determined the quality of the coatings using surface micrographs and X-ray structural analysis. X-ray diffraction studies were performed on a Dron-3 diffractometer in CuKα radiation. The study of the surface morphology of the coatings was performed on an electron microscope. The deposition rate of copper was determined by the gravimetric method, and the stability of solutions of chemical copper plating was evaluated by the “Trigger” method [9].

3. Research of the complex formation processes in the system Cu(II) - HEDP - H₂O

In the study of metal deposition processes, it is necessary to know the composition and stability of the resulting complexes, their structure, and the symmetry of the nearest environment. The literature data on the complexation of copper (II) with hydroxyethylidene diphosphonic acid is inconsistent and does not provide a complete picture of the composition and stability of the resulting complexes. In addition, the study of complex formation equilibria was carried out in the pH range up to 10. In this connection, it seems necessary to study the complex formation processes of Cu (II) with HEDP in a wider pH range in order to develop promising technological processes for the deposition of copper coatings.

Five-basic hydroxyethylidenediphosphonic acid (HEDP, H₅L) has the structure:
OH OH OH

0 = P – C – P = 0

OH CH₃ OH

To study the composition and structure of Cu (II) complexes with HEDP in aqueous solutions with an acidity varying from 0.5 to 13, we used the EPR method [10]. The parameters of the EPR spectra finely react to changes in the composition of the coordination sphere of the metal–complexing agent. A consistent increase in pH during the transition from acidic to alkaline (the step of pH change was 0.2 ... 0.5) in the system Cu(II) - HEDP - H₂O allows us to clearly record systematic and reproducible changes in the parameters and form of the EPR spectra during the formation of various forms complexes (table 1).

**Table 1.** Parameters of the EPR spectra of copper (II) complexes with HEDP in vitrified solutions (77K) at various pH values.

| pH   | Parameters of EPR spectra | \( g_\| (\mp,0.003) \) | \( g_\perp (\mp,0.003) \) | \( A_\| (\mp,1) \), Oe | \( g_\theta (\mp,0.003) \) |
|------|---------------------------|-------------------------|-------------------------|------------------------|-------------------------|
| 0.5  |                           | 2.420                   | 2.057                   | 127                    | -                       |
| 1-5.5|                           | 2.430                   | 2.065                   | 119                    | -                       |
| 1-6  |                           | 2.430                   | 2.066                   | 124                    | -                       |
| 1-2  |                           | -                       | -                       | -                      | 2.19                    |
| 6-9  |                           | 2.400                   | 2.053                   | 128.5                  | -                       |
| 6-7.5|                           | -                       | -                       | -                      | 2.17                    |
| 10-12|                           | 2.390                   | 2.045                   | 133.5                  | -                       |

In the system Cu (II) - HEDP - H₂O at pH 0.5 for excess of ligand and in the range of pH 0.5 ... 1.3 for lack of ligand, the shape and parameters of the EPR spectra correspond to the copper aqua complex. Above of these pH values we can note the participation of various forms of HEDP in complexation with copper (II). In the acidic pH range, we can observe an anisotropic spectrum with components of a hyperfine structure resolved in parallel orientation, characterized by a decrease in the constant \( A_\| \) and an increase in \( g_\| \) and \( g_\perp \) (\( A_\| = 119 \) Oe, \( g_\| = 2.430, g_\perp = 2.065 \)) compared to similar values of parameters for aqua copper. Changes in the parameters of anisotropic EPR spectra for complexes formed in the acidic region indicate the hardening of axial bonds of copper with ligands. Based on our data, we can assume that in the acidic region under conditions of lack of ligand, a complex of the composition \([Cu(\text{H}_2\text{L})\text{]}\) is formed, and with an excess of ligand - a complex of the composition \([Cu(\text{HL})\text{]}\)²⁻. The intensity of the spectra corresponding to this complex is maximum at pH 3. In the pH range 3.5 ... 5.5, the formation of insoluble complexes occurs. With an excess of ligand, starting from pH 6, the intensity of the EPR signal in solution increases dramatically, which indicates the formation of new types of soluble complexes. For a pH value of 9, \([Cu(\text{HL})\text{]}\)²⁻ with an anazotropic spectrum parameters prevail in the solution: \( g_\| = 2.400; g_\perp = 2.053; A_\| = 128.5 \), and the range of pH 10 ... 12 forms complexes \([Cu(\text{HL})\text{]}\)⁶⁻, which give anazotropic spectra with the following parameters: \( g_\| = 2.390; g_\perp = 2.045 \); and \( A_\| = 133.5 \). A decrease in \( g_\| \), \( g_\perp \) and an increase in \( A_\| \) in the spectra of these complexes in comparison with similar parameters of the spectra of the aqua complex and the \([Cu(\text{HL})\text{]}\)⁰, \([Cu(\text{HL})\text{]}\)²⁻-complexes indicate an increase in planar bonds of copper with ligands. The intensity of the EPR spectrum due to the accumulation of the complex particle \([Cu(\text{HL})\text{]}\)⁶⁻ is maximum at pH 11, and then the signal intensity decreases from pH 11.5, which may indicate the formation of binuclear complexes. Since the literature data on the composition and stability of the resulting complex ions in the alkaline region (pH 9 ... 13) is not available, we performed the simulation of equilibrium processes in the Cu (II) - HEDP - H₂O system based on the EPR data. Using the CPESSP software we processed the experimental dependence \( I = f(pH) \), where \( I \) is the intensity of the EPR signal, and
obtained the formation equilibrium constants and the stability constants of the identified complex forms. The calculation results are shown in Table 2.

**Table 2.** The equilibrium constants of formation \((K_p)\) and stability \((\beta)\) of copper (II) complexes with HEDP (L).

| Complex                  | \(\log K_p\) | \(\log \beta\) |
|--------------------------|--------------|----------------|
| \([\text{Cu}(HL)_2]^{6-}\) | -29.5        | 16.44          |
| \([\text{Cu}_2(HL)_2]^{4+}\) | -20.04       | 25.9           |
| \([\text{Cu}_2(HL)L]^{3-}\) | -28.71       | 29.23          |
| \([\text{Cu}_2L_2]^{6-}\)     | -39.52       | 30.42          |
| \([\text{CuL}]^{3-}\)         | -21.65       | 13.32          |
| \([\text{Cu}_2L(OH)]_2^{3-}\) | -33.25       | 29.72          |

4. **The study of chemical deposition of copper from solutions based on HEDP**

The literature has just a limited information on the use of organophosphorus ligands, including HEDP, in metal plating processes. Practically, there is no information about the properties and quality of the coatings obtained, it says only about the high stability of the solutions. Since we studied the complexation of copper (II) with HEDP, it is of practical interest to research the possibility of obtaining copper coatings from solutions based on HEDP. It should be noted that this ligand is non-toxic and available on an industrial scale.

We chose the process of chemical copper plating for the study. It is currently widely used in practice to obtain an electrically conductive copper sublayer and an independent copper coating on dielectrics. However, popular in the production of chemical copper plating solutions have insufficient stability and not always the coating turns out to be of good quality. In addition, the ligands used (tartrate, trilon B) are scarce. Depending on the composition and structure of the complex being formed, it is possible to obtain different rates of copper recovery on the catalytic surface of the dielectric and metal, different solution stability and different physicochemical properties of the depositions.

In the study of the complex formation of copper (II) with HEDP, we found that in strongly alkaline solutions copper (II) ions are present mainly in the form of \([\text{Cu}_2L_2]^{6-}\) in the Cu (II) - HEDP - \(H_2O\) system.

We determined the stability constants of the resulting complexes: \([\text{Cu}_2L_2]^{6-} = \log \beta = 30.42\). If we compare copper complexes with HEDP with trilonate complexes (\(\log \beta = 21.1\)), traditional in solutions of chemical copper plating, it turns out that copper complexes with HEDP are the most stable, which probably causes the high stability of copper plating solutions based on HEDP.

The experiments were carried out with copper-plating solutions containing (mol/l): \(\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \to 0.1\); ligand (HEDP) - 0.2; formaldehyde - 0.3; \(\text{NaOH}\) – up to pH 12.8. The coatings were deposited at a temperature of 25°C for 0.5 hours on samples of ABS-plastic, previously degreased, etched and activated by well-known methods [11]. The loading density was 2 \(dm^2/l\). The deposition rate was determined by the weight gain, and the stability of the solutions was determined by the “Trigger” method [9]. The following data were obtained: deposition rate - 1.5 \(\mu m/h\); stability - 47.9 min; the appearance of the coating is light pink.

Experiments have shown that uniform, fine-crystalline and dense depositions of copper, with good adhesion to the base, can be obtained from solutions with HEDP, although the speed of deposition is not very high. The peculiarities of the copper plating process in a solution with HEDP are its high stability, good coating quality of light pink color resembling electroplating copper. It is known that the properties of copper deposits, as well as the properties of metallic coatings of a different nature, are determined by their structure. Therefore, after the deposition from solutions of chemical copper plating, the depositions were subjected to phase-structural studies.

Figure 1 shows the line X-ray diffraction patterns of annealed copper samples (as a reference) and coating from HEDP solutions. They show that practically pure copper with a lattice period of 0.3607
nm is deposited from a solution based on HEDP. However, both solutions have growing crystals oriented along the 111 face.

Figure 1. X-ray diffraction patterns: a – annealed copper; b – deposition of copper from solutions of chemical copper plating based on HEDP.

Radiographs also show some small peaks, corresponding to impurities of copper (I) oxide and copper (II) oxide. The magnitude of these peaks was approximately at the noise level and it was not possible to quantify the content of copper oxides on the surface or in the bulk of the coating.

We also carried out an electron microscopic study of the surface structure of copper deposits. The data obtained indicate that the surface of copper is an even crystalline deposition.

The problem of stability and repetitive use is relevant for a solution of chemical copper plating. Therefore, we also tested the effect of some additives. When choosing a stabilizing additive, we relied on the experience of stabilization of chemical metallization solutions. The literature tells that organic compounds containing a trivalent nitrogen atom and bivalent sulfur, capable of adsorption bonding to the metal surface (as a result of formation of a chemical bond between lone electron pairs and free d-orbitals of the metal), are the most promising for stabilizing solutions of chemical copper plating. In addition to electronic factors, the effectiveness of the additive is determined by its stereochemistry — the ability of adsorbed additive molecules to block a large number of active sites of the catalyst [12–15].

We evaluated the effect of additives of various types on the process of copper (II) reduction from complexes with HEDP: I - 1-ethylthiobenzylphosphonic acid; II, III - ammonium salts of 1-ethylthiobenzylphosphonic acid; IV - morpholine; V - N-phenylamide-1-phenyl-1-N-
morpholinomethanesulfonic acid (Table 3). We should note that additive IV is recommended in the literature [16-18] as a stabilizer for copper plating solutions, and the effect of other additives was tested for the first time. We investigated the effect of additives on the stability of the solutions, the deposition speed and the appearance of the coatings (Table 3).

Table 3. Effect of additives on the process of copper plating.

| Additive, | Deposition speed, [10^-5 mol/l] | Stability, [µm/h] | The appearance of the coating |
|-----------|-------------------------------|-----------------|-----------------------------|
| I         | 1.5                           | 49.1            | light pink                  |
| II        | 1.5                           | 41.4            | light pink                  |
| III       | 1.5                           | 42.7            | light pink                  |
| IV        | 1.2                           | 48.5            | light pink                  |
| V         | 1.4                           | 49.8            | light pink                  |

Studies have shown that additives have different effects on the process of copper plating. Additives I and V are of the greatest interest. Additives II – IV have little effect on the stability of the solution and have virtually no effect on the deposition rate. If additives I and V are used as stabilizing substances, solution stability can be achieved.

On the basis of the stabilizing additive I (I - ethylthiobenzylphosphonic acid) in the Cu(II) – L – CH2O system, where L is HEDP, we carried out experiments to identify the optimal conditions for the chemical deposition of copper. As a result of studying the influence of the concentration of the main components, pH and temperature on the quality of the copper deposition, as well as the deposition speed and the stability of the solution, we selected the optimal solution composition [mol / l]:

- Copper (II) sulfate
- Hydroxyethylidenediphosphonic Acid
- Formalin
- I – ethylthiobenzylphosphonic acid
- Sodium hydroxide

The study of the influence of the concentration of the additive on the deposition speed and the stability of the solution showed that the optimal concentration lies in the range 1 \cdot 10^{-5} - 2,5 \cdot 10^{-5} mol / l. Raising the concentration of the additive above these values increases stability, but at the same time the speed of copper deposition decreases sharply. A solution of this composition at a temperature of 18-25°C can give a pink, dense, fine-crystalline depositions of copper on dielectric products.

In the study of the complex formation of copper (II) with HEDP, we found that in strongly alkaline solutions copper (II) ions are present mainly in the form of [Cu2L2]^6− in the Cu(II) – HEDP – H2O system. We determined the stability constants of the resulting complexes: [Cu2L2]^5− - lgβ = 30.42. If we compare copper complexes with HEDP with trilonate complexes (lgβ = 21.1), which are traditional in solutions of chemical copper plating, it turns out that copper complexes with HEDP are the most stable, which probably leads to high stability of copper plating solutions based on hydroxyethylidenediphosphonic acid.

5. Conclusion
We used the electron paramagnetic resonance method to study the formation of copper (II) complexes with hydroxyethylidene diphosphonic acid. Then we determined the stability constants of the complexes and their regions of existence. Moreover, the study shows the possibility of obtaining high-quality copper coatings from solutions of chemical copper plating based on HEDP. X-ray structural analysis of the samples showed that there is a deposition typical for pure copper with a slight difference in the broadening of the peaks, which is associated with the grain sizes of copper crystals. The research established that hydroxyethylidene diphosphonic acid forms stable complex compounds with copper (II) ions and is a promising ligand for obtaining high-quality metallic coatings.
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