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MODIFICATION OF WATER POLYMER COMPOSITIONS FOR ELECTRODEPOSITION OF METALLOPORPHYRINS*

G.N. Bespalova@, A.N. Larin, T.A. Ageeva, O.I. Koifman, A.K. Morokhina, K.E. Moiseeva

Ivanovo State University of Chemistry and Technology,
SRI of Macroheterocyclic compounds, Ivanovo, 153000, Russia
@ Corresponding author e-mail: kraska@isuct.ru

It is known that coatings produced by electrodeposition, cured at high temperatures (180°C and above).The aim of this study is reducing the energy intensity of production of polymer coatings, improving physical, mechanical properties of the polymer coatings and expansion of colors of paints for the electrodeposition.

As the object of study was chosen lacquer KCh-0125, the main component of which is maleated polybutadiene. A micelle of film-forming neutralized tertiary amine is a colloidal particle size of 40 to 70 nm. One of the most effective and low-cost ways to the above problems is the introduction of the water-based oligomeric compositions hydrophobic modifiers. As modifiers were selected naturally occurring metalloporphyrins – cobalt (II) complex of pheophytin a (CoPh) and copper (II) complex of methylpheophorbide a (CuMPP). The method of introduction of the CoPh and the CuMPP of the water-based compositions for electrodeposition was developed. Colloid-chemical properties of the resulting compositions were studied. It was presented the most probable structure of the scheme colloidal particles modified by metalloporphyrins. It was conducted viscometric, spectral studies; the method of dynamic light scattering was used to determine the zeta potential and the size of colloidal particles.

It was demonstrated high catalytic activity of metal complexes of porphyrins examined in structuring processes electrodeposited coatings when cured. Introduction of metalloporphyrins in the coating helps to reduce the curing temperature to 160°C. This makes it possible to reduce or duration, or a temperature curing coatings. The introduction of CuMPP make possible to obtain transparent coatings emerald green. Modified electrodeposited coatings also have good water and salt resistance.

Keywords: *electrodeposition, modification, metalloporphyrins, colloidal solution, colloidal particle, the properties of the solutions, the properties of the coatings.*

Introduction

One of the main tendencies of development of the modern paint-and-varnish industry is the aspiration to reduce or completely exclude the application of toxic, fire-dangerous and rather expensive organic solvents. This led to the creation of water-base materials, powdered paints and paint-vehicle systems which are polymerized directly on the protected surface.

The basic purpose of polymer coatings is to protect metal products against corrosion and make them look beautiful. Realizing the protective anticorrosive potential of polymer paint coatings most completely is possible when using a modern way of painting – electrodeposition.

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The method of directed motion of charged particles or macroions was discovered more than two centuries ago, but its use in technology did not start before 1960-ies, when special filmogens – oligomeric polyelectrolytes – were synthesized. However, the range of such materials is small up to the present day. One of serious shortcomings of the materials offered in the market is high temperature of formation of coatings based on them (180–200°C). The use of such temperatures, on one hand, causes increased power consumption of technologies and, on the other hand, limits the range of application of water-base materials of light tones, because coatings on their basis cured in such conditions get a yellow tint.

In this regard decrease in power consumption of obtaining polymer coatings, improvement of their physicomechanical characteristics and expansion of color set of paints and varnishes applied by electrodeposition are actual problems of modern technologies.

One of effective and low-cost solutions of these problems is to introduce target modifying additives into oligomeric water-base compositions. In this study we chose metalloporphyrins of natural origin as such modifiers [1].

Due to a set of physical and chemical properties porphyrins and their analogs attract interest of researchers in chemistry, biology, medicine, optics etc. The existence of double bonds, chromophoric and auxochrome groups in their molecules gives them the ability of painting polymer coatings. At the same time, the presence of polyvalent metals, such as cobalt, copper and others, gives ground to assume that metalloporphyrins can show catalytic activity in the oxidative polymerization of nonsaturated filming agents when curing coatings.

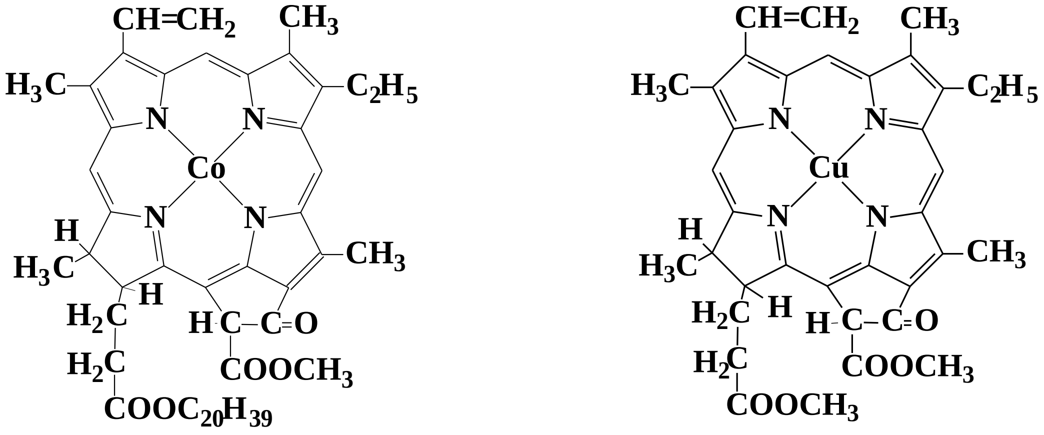
One of important properties of micellar systems is their ability of solubilizing hydrophobic substances. This property was initially a basis for the development of technology for introducing water-insoluble modifiers – metalloporphyrins – into water-base compositions (micellar by the nature) containing oligomeric filming agents-polyelectrolytes [2].

A simplified scheme of the structure of a micelle of partially neutralized filming agent applied by electrodeposition from water-base compositions can be presented as follows:

$$[mR(COOH)_{\alpha}\times nR(COO^{-})_{\alpha}(n\alpha - x)\times R'_{3}N^{+}H]^{x-}xR'_{3}N^{+}H,$$

where $R(COOH)_{\alpha}$ is a water-base filming agent, $R'_{3}N$ is a trialkylamine (neutralizer).

KCh-0125 varnish was chosen as a model filming agent for anode electrodeposition. Its main component is oligomeric maleinized polybutadiene. Such metalloporphyrins as cobalt(II) pheophytin *a* complex (CoPh) and copper(II) methylpheophorbide *a* complex (CuMPP) (Figure 1) were used as modifiers.



a)

b)

Figure 1. Modifiers of water-base compositions: *a)* CoPh; *b)* CuMPP.

When introducing any additives into water-base compositions applied to painted electrically conductive surfaces by electrodeposition, it is necessary to satisfy a number of specific requirements. In particular, the additives introduction should not change (within strictly determined limits) the properties of the water compositions: conductivity, pH, dispersive capacity, aggregative and sedimentative stability. Obviously, the smallest influence on these properties of oligomeric compositions is observed when the water-insoluble modifiers are introduced into the hydrophobic core of the filming agent micelle $R(COOH)\alpha$, and not when they are in the aqueous phase of the composition. In this case proportionality of their working with the oligomeric filming agent is attained. This provides constancy of the filming agent : modifier ratio during the whole usage time of the composition [3].

In order to develop a technology for the preparation of aqueous modified compositions having good efficiency and high stability various methods of introducing water-insoluble metalloporphyrins into work solutions for electrodeposition were tested. It was found that the optimal method is to introduce the modifiers in the form of their solutions in organic solvents immiscible with water in concentration no more than 10^{-4} g/l.

Experimental

Solutions for the tests were prepared as follows.

Preparation of a model composition (comparison composition) for 100 g of work solution. A neutralizer – 1.0 ml of ammonium hydroxide (or 0.7 ml of triethylamine) – is added to 10 g of KCh-0125 varnish. The mixture is thoroughly stirred for 10 min. Then distilled water is added in small portions under continuous stirring until the total mass of 100 g is attained. After the addition of the whole amount of water the composition is stirred for 10 min, and its uniformity is visually checked.

Preparation of a modified composition for 100 g of work solution. A solution (1 ml) of a metalloporphyrin (cobalt(II) pheophytin *a* complex or copper(II) methylpheophorbide *a* complex is added to 10 g of KCh-0125 varnish. The mixture is stirred for 10 min. Then a neutralizer – 1.0 ml of ammonium hydroxide (or 0.7 ml of triethylamine) – is added. After stirring for 10 min distilled water to is added to attain the total mass of 100 g.

For studying the properties of the obtained compositions with concentrations 0.03125–8.00000 g/dl the following methods were used:

– viscometry of the solutions (Ostwald viscometer);

– measurement of the solutions pH (pH/ORP Meter HI 2211);

– diffuse reflection spectroscopy (SHIMADZU UV-2550 PC spectrophotometer);

– photon correlation spectroscopy (Zetasizer Nano ZS).

Painting was carried out with the use of an anode electrodeposition installation at a constant voltage.

In order to study the properties of the obtained electrodeposited coatings standard techniques were used:

– determination of the unit weight of the coatings (electronic weighing unit produced by Development Design Office "VESTA");

– determination of the degree of cure of the coatings by the content of gel-sol fraction in them (Soxhlet extractor; the method is based on the ability of the soluble part of a coating – sol-fraction – to be washed away by a solvent and consists in quantitative determination of the content of the sol fraction not bonded in a polymeric network – gel fraction);

– determination of the wear resistance of paint coatings (it is estimated by the mass of quartz sand required for the destruction of the coating up to the substrate by a stream of quartz sand falling onto the coating from a certain height);

– determination of the bending elasticity of the coating (GOST 6806-73);

– determination of the impact strength of the coating (GOST 4765-73);

– determination of the water resistance, salt resistance and alkali resistance of the coating (by immersion into water, a 3% solution of sodium chloride or 3% solution of sodium hydroxide, respectively);

– determination of the coating adhesion (GOST 15140-78).

Results and Discussion

Comparative reflection spectra of water-base compositions without modifiers and with modifiers recorded on a SHIMADZU UV-2550 device (Japan) show an inclusion of CoPh (λ = 652 nm) and CuMPP (λ = 672 nm) in the filming agent in the working compositions used at electrodeposition (Figure 2).

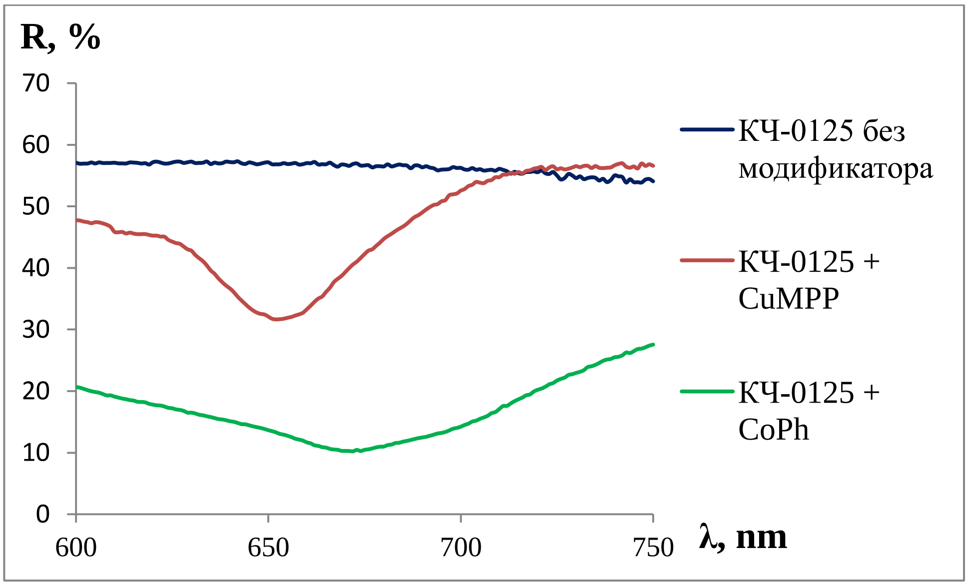


Figure 2. Comparative reflection spectra of water-base compositions.
[КЧ-0125 means KCh-0125; без модификатора means without modifier]

In order to study the suitability of the obtained compositions for electrodeposition dependences of the change in the unit weight of the coatings (thickness) on voltage and electrodeposition time were studied. The study showed that good-quality coatings are obtained in the range of voltage 60 – 90 V (Figure 3). When voltage is decreased to 30 V, thin coatings not providing sufficient anticorrosive surface protection are obtained. Increasing voltage to 120 V results in the appearance of reprecipitation defects (beads). Increasing electrodeposition time (Figure 4) from 30 to 90 s increases the unit weight of the coatings by a factor of 1.5 to 1.7, and the quality of the coatings remains good. Changing the values of voltage and paining time in the specified range enables regulating the coatings thickness from 7 – 8 to 20 – 25 μm, which allows using them for the protection of products of different purpose.

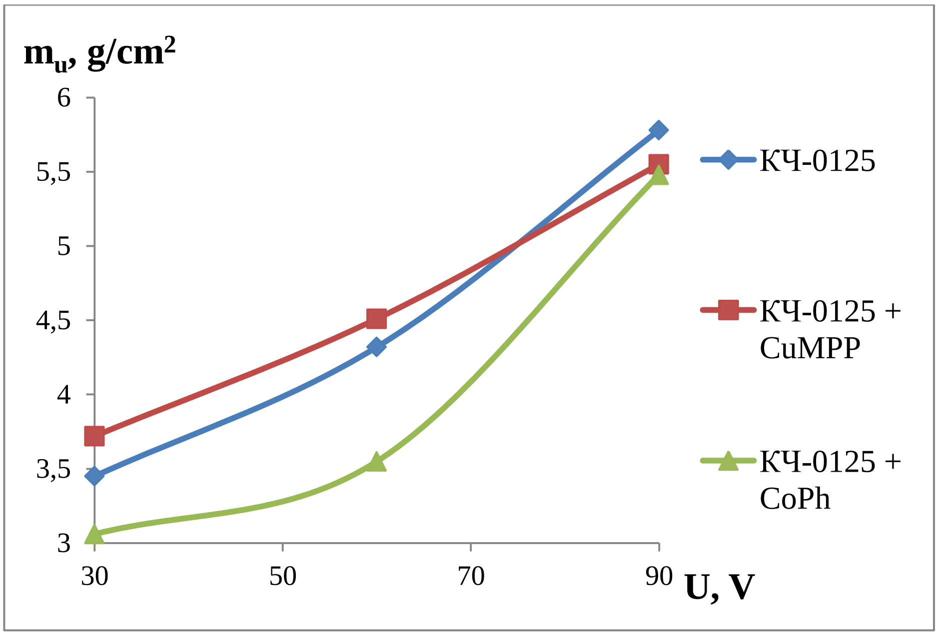


Figure 3. Dependence of the unit mass of the coatings on voltage.

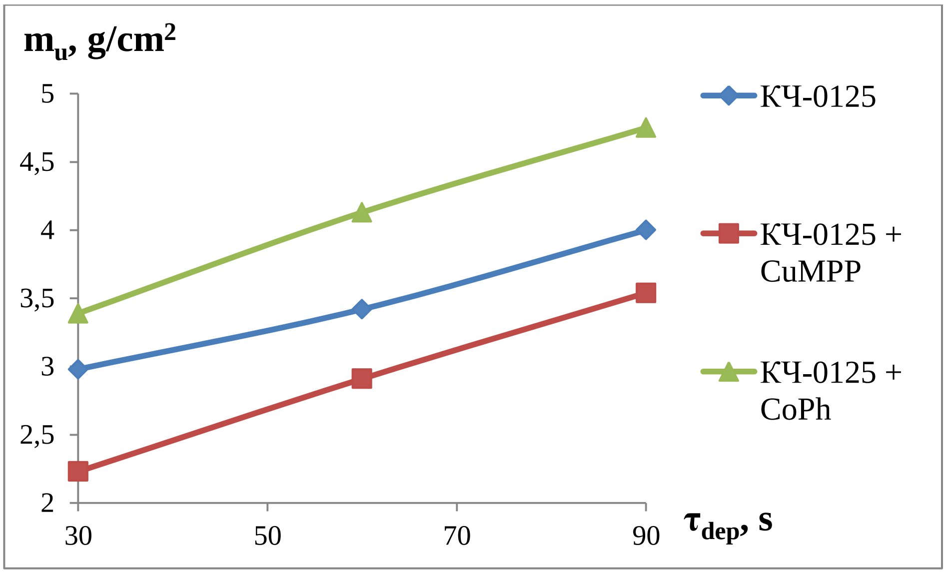


Figure 4. Dependence of the unit mass of the coatings on deposition time.

Colloidal systems having a large specific surface and a large free energy are essentially nonequilibrium systems. Obviously, they will always tend to the equilibrium state, where the system is divided into 2 phases with the minimum boundary surface (although this equilibrium practically may never be attained).

The compositions studied by us belong to such disperse systems. Therefore, topics related to studying their stability are important for the creation of materials intended for electrodeposition. Studying the aggregative stability of water compositions by changes of their optical density in time showed that no increase in the size of colloid particles occurs for more than 6 months. This proves the high aggregative stability of modified film-forming systems.

Another important indicator determining the stability of colloidal systems, as well as their electrophoretic mobility, is the value of ζ-potential. Comparative studies of the ζ-potential of modified and unmodified compositions were carried out with the use of a ZetaSizerNano ZS device.

The concentration dependence of changes in the ζ-potential of all the studied compositions practically coincides (Figure 5).

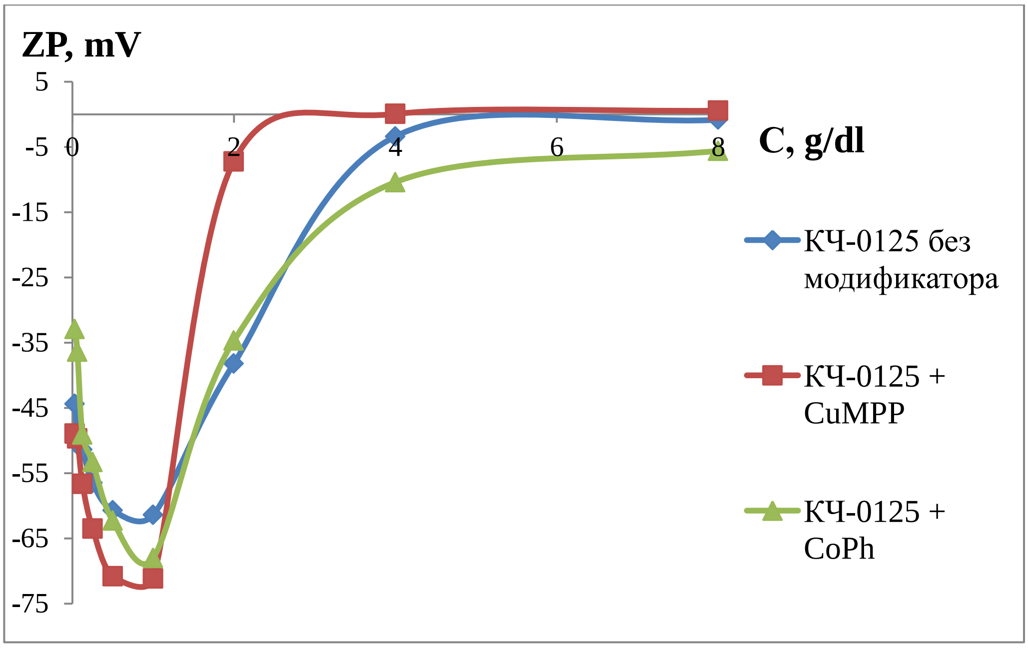


Figure 5. Dependence of changes in ζ-potential on the solution concentration.

When diluting the solutions to concentration 0.5 – 1 g/dl, the negative value of ζ-potential grows to its maximum values: 61 mV for the solution of pure KCh-0125 and from –68 to –71 mV for the modified compositions. Some growth of the absolute value of ζ-potential for the modified compositions, apparently, is due to an increase in the micelle core. In this case, stabilization of a colloid particle requires a larger amount of carbanions, which results in the growth of the negative charge. Further dilution leads to a decrease in the effective charge of the particle, probably due to its disaggregation.

The dependence of the change in the solutions pH upon dilution pH = f(C) has also an extremal character (Figure 6).

Dilution with water results to a restructuring of the micelle. Consequently, its diffusion layer extends. This promotes the transition of an increasing number of antiions R'_3N^+H from the adsorption layer into the diffusion one. Their concentration in the dispersion medium increases. At the same time the number of free charges of carbanions $RCOO^-$ on the micelle surface increases.

When interaction with water occurs, partial regeneration of carboxyl groups of very weak oligomeric polyacids of the filming agent is possible:

$$RCOO^- + H_2O = RCOOH + OH^-,$$

which leads to the increase in the solution pH value upon dilution (Figure 6).

A similar dependence of pH change on concentration is observed in case of using copper methylpheophorbide *a* complex as a modifier (Figure 6).

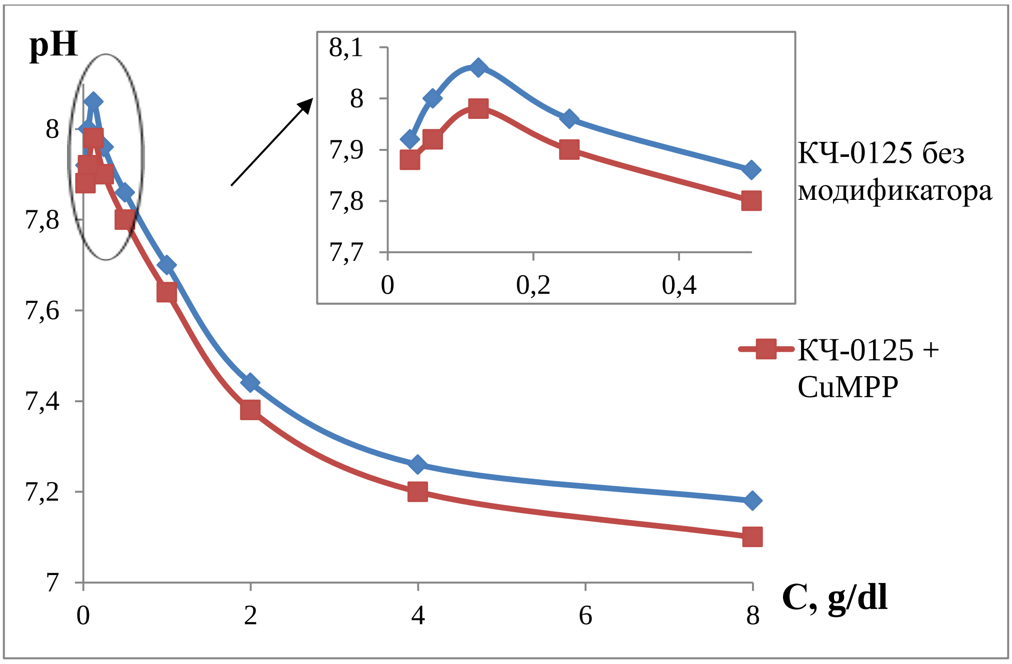
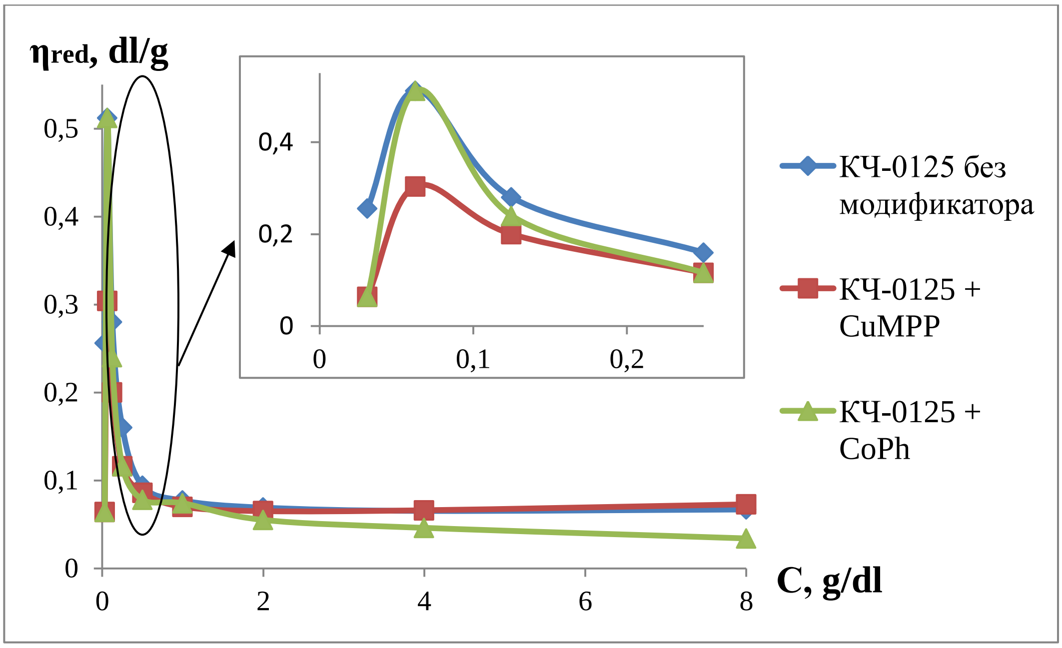


Figure 6. Dependence of pH of aqueous solutions of filming agents on their concentration.

This proves that the hydrophobic modifier located in the micelle core does not affect the changes of the mentioned parameters. In this case the latter are completely determined by the properties of KCh-0125 filming agent functioning as a charger and stabilizer of the colloid particle. Small divergences in the absolute value of the maximum pH growth at low concentration of the solutions can indicate only the specificity of the interaction (coordination) of the filming agent and the concrete modifier in the micelle core.

It is known that, when diluting solutions of nonionic polymers, the dependence of reduced viscosity $\eta_{red} = \eta_{spec}/c$ on the solution concentration is linear: $\eta_{spec}/c = a+bc$. The properties of solutions of polyelectrolytes considerably differ from those of solutions of nonionic polymers. Such systems including solutions based on KCh-0125 are characterized by progressing increase of reduced viscosity upon dilution (Figure 7). As shown by research, their introduction into the composition of modifying additives of metalloporphyrins does not affect the abnormal nature of the solutions behavior.

Such a type of dependence is caused by the fact that diluting the solution increases the volume in which antiions of the micelle R'_3N^+H are distributed. This leads to reduction of shielding of ionogenic group of $R(COO)^-_\alpha$ macromolecules and, consequently, to strengthening of their mutual repulsion and, as a result, to unfolding of chains of macroanions, i.e., to an increase in the "effective" volume of the micelle. This is so-called "polyelectrolytic effect". The maxima of the values of reduced viscosity on $\eta_{red}/c = f(c)$ curves (Figure 7) correspond to the maximal effective volume occupied by the colloid particle in these conditions of measurement. Further dilution results in the linear decrease of reduced viscosity of the solutions typical of the classical Newtonian current [5].



Figire 7. Dependence of reduced viscosity on the solutions concentration.

Studies on the concentration dependences of changes in ζ-potential, solution pH and reduced viscosity η_{red}/c showed that they have the appearance typical of colloidal systems. Their behavior is determined by the properties of maleinized polybutadiene (filming agent). The latter is a charger and stabilizer of the colloid particle.

All this allows suggesting the most probable scheme of the structure of the colloid particle of the water-base filming agent. This scheme includes the studied modifiers exactly in the hydrophobic core (Figure 8).

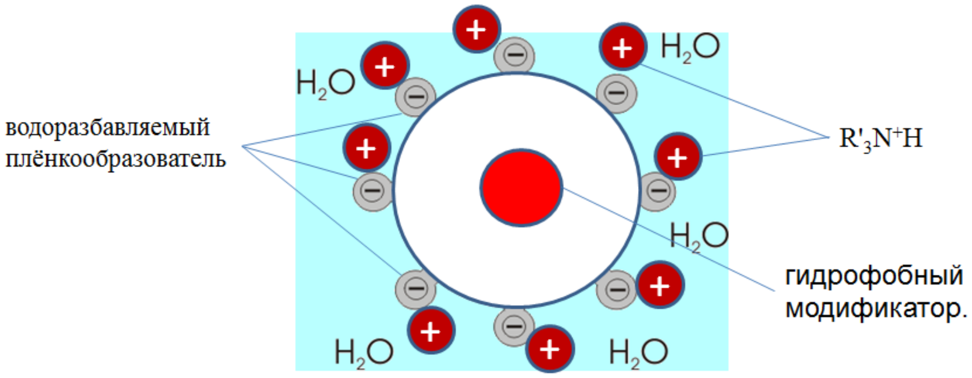


Figure 8. Scheme of the structure of a micelle of the modified filming agent. [водоразбавляемый плёнкообразователь meanswater-base filming agent; гидрофобный модификатор means hydrophobic modifier]

The study on the catalytic activity of cobalt(II) pheophytin *a* complex and copper(II) methylpheophorbide *a* complex upon curing the electrodeposited coatings was carried out with the use of determining the content of the gel (G) fractions of the coatings in a Soxhlet apparatus.

It is known that metalloporphyrins have the unique ability of coordinating the molecules of other substances around them. Due to this ability they can have catalytic impact on the course of chemical processes, in particular, oxidation-reduction [4].

As mentioned above [3], it is precisely these processes that are generally responsible for the formation of polymer coatings based on the polybutadiene filming agent.

Comparative results of the determination of the value of the gel fraction of coatings cured at 180 and 160°C are presented in Table 1.

Table 1. Effect of metalloporphyrins on the curing of electrodeposited coatings

Curing modes		Content of G fractions (%) in coatings based on:		
Temperature, °C	Time, min	KCh-0125	KCh-0125 + CuMPP	KCh-0125 + CoPh
180	30	83.5	87.9	96.1
160	30	57.5	79.2	93.1

The study shows the possibility of using the mentioned metalloporphyrins as catalyzing agents in water compositions for electrodeposition. It was found that the greatest catalytic activity is shown by CoPh.

The increase of the gel fraction of the coatings from 57 – 84% to 93 – 96% (Table 1) indicates the deepening of the processes of structuring of the electrodeposited films obtained from compositions with cobalt pheophytin *a* complex at the identical modes of curing.

The catalytic activity of the studied metalloporphyrins is confirmed also by the research results presented in Figure 9.

The obtained data show a considerable increase of the rate of curing films containing CoPh. In the first 15 min of curing the G fraction content in these coatings is 92% as compared to 42 and 61% for the unmodified coatings and coatings containing copper pheophorbide, respectively (Figure 9).

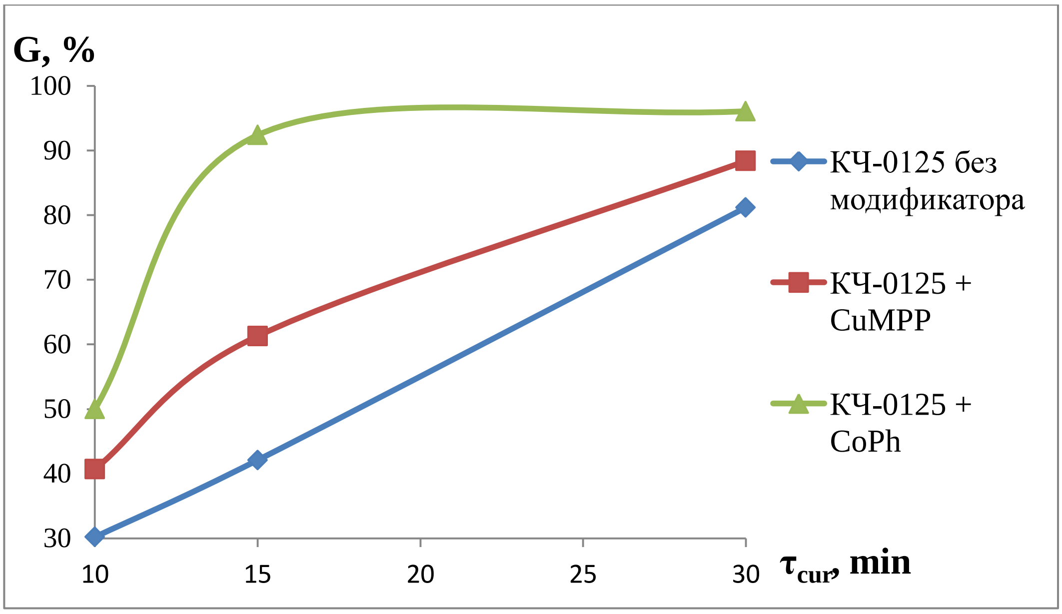


Figure 9. Change in the G fraction content in the process of electrodeposited films curing (curing temperature: 180°C).

Tests of the cured coatings were carried out according to the standard techniques applied in the paint coatings technology.

Results of studying the physicomechanical and protective properties of the coatings are presented in Table 2.

The time of curing at the high-temperature mode (180°C) should be reduced at least to 15 min. Otherwise deeply cross-linked coatings are obtained, which has an adverse effect on their physicomechanical properties, in particular, on the film bending strength (Table 2).

Table 2. Effect of metalloporphyrins on the physicomechanical and protective properties of electrodeposited coatings

Composition of paint coating	Impact strength, cm	Bending strength, mm	Durability, rel. units	Salt resistance, h	Water resistance, days	Alkali resistance, h
Curing mode: 180°C, 30 min						
KCh-0125	50	1	1.0	no more than 120	more than 30	no more than 120
KCh-0125 + CuMPP	50	1	1.5	no more than 240	more than 30	no more than 120
KCh-0125 + CoPh	50	3	1.8	more than 240	more than 30	no more than 168
Curing mode: 160°C, 30 min						
KCh-0125	50	1	1.0	no more than 24	more than 30	no less than 72
KCh-0125 + CuMPP	50	1	1.3	no more than 120	more than 30	no less than 72
KCh-0125 + CoPh	50	3	1.6	no more than 48	more than 30	no less than 48

Conclusion

A technique for introducing cobalt(II) pheophytin *a* complex and copper(II) methylpheophorbide *a* complex into water-base compositions was developed for electrodeposition. The colloid-chemical properties of the obtained compositions were studied. The most probable scheme of the structure of the colloid particle modified by metalloporphyrins was suggested. High catalytic activity of the studied metal complexes of porphyrins in the structuring of electrodeposited coatings at their curing was shown. This enables to reduce the duration or temperature of the coatings curing and to reduce considerably the power consumption of the production.

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