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Electrophoretic-electrochemical Deposition of Polymers and Metals

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The physicochemical principles of the formation of composite polymeric and metallopolymer coatings by the electrodeposition of polymer dispersions in water and electrolyte solutions are described. The electrophoretic and electrophoretic-electrochemical mechanisms for the formation of the polymer and metallopolymer coatings are examined. The role of the chemisorption interaction of the polymers and colloidal metals in increasing the protective properties of the coatings is demonstrated. The new phenomenon of "electrophoretic" polarisation and its influence on the electrode processes are considered.
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I. INTRODUCTION

The use of electric fields to form dispersed structures has been acquiring increasing importance. Particles can be oriented in electrical fields along their geometrical or molecular axes and directional movement of the particles and the interaction of polarised particles leading to structure formation can be achieved. These effects are used in electrodeposition processes,[1-4] in the manufacture of materials with anisotropic properties,[5] in the purification of liquids by electrofiltration,[6] and for controlling the mechanical properties of dispersed systems.[7]

The use of electric fields to create composite materials and coatings has opened up wide possibilities. Together with the rapid development of traditional fields of electrotechnology such as electroplating and galvanoplastics, the formation in the electric field of composite coatings based on polymers, metals, and non-metals is being applied to an increasing extent in this type of technology.

Three main trends can be distinguished in this field. The process involving the formation of coatings from solutions of oligomeric electrolytes in a constant electric field—the electrodeposition method—was developed at the beginning of the 1960's.[1-3] It is based on the formation in the electric field of a water-insoluble deposit on the anode and its subsequent thermohardening with formation of a three-dimensional polymer network from the oligomer. The mechanism of the formation of films bound by adhesion to a support includes also the formation of local bonds between groups of polymer molecules and the surface of the support.[4,5]

Numerous studies designed to create combined electrochemical coatings, which are compositions consisting of metals, alloys, and substances dispersed in them, were carried out in the same period.[6,7] The dispersed substances are refractory borides, carbides, nitrides, silicides, graphites, carbonaceous materials, abrasive powders, and lubricants. The coatings are formed as a result of the electrolytic segregation of the metal (matrix), the parallel processes involving the adhesion of the particles of the disperse phase to the matrix and their growth into the latter.

In recent years, there has been a sharp increase of interest in electrophoresis as a method of preparation of coatings formed from dispersions of various substances—polymers, metals, oxides, and natural materials.[8-12] The possibility of the simultaneous deposition and orientation of particles of different nature in order to obtain composite and especially metallopolymer coatings is of special interest.[13,14]

The introduction of colloidal metals into polymers, accompanied by the chemisorption interaction of the macromolecules with the active centres on the surfaces of the colloidal metal particles, leads to the formation of metallopolymers.[15,16] Two-phase systems stable as regards aggregation, in which the metal is uniformly distributed within the polymer, arise under these conditions. The character of the interaction of the macromolecules with the surfaces of the highly dispersed particles is determined by the chemical nature of the polymer and the metal. The macromolecules can be distributed on the surfaces of metals in the form of fixed adsorption layers, forming covalent, ionic, and coordinate bonds with the surface metal atoms.[17,18]

The formation of metallopolymer coatings in the electric field is based on the simultaneous occurrence of two processes—the electrophoretic deposition of polymer dispersions (solutions) and the electrolytic segregation of colloidal metals or alloys.[19-21] The successful development of this important branch of the electrotechnology of coatings has been promoted by fundamental studies in colloid chemistry during recent years. The creation of a theory of the polarisation of the electrical double layer and of its kinetic model, the development of a theory of the stability and coagulation of colloidal systems in an electric field, and the prediction and discovery of a number of new non-equilibrium electrokinetic phenomena—dipolophoresis, diffusiophoresis, and non-linear electrophoresis[22-26]—should be included among them.

The above theoretical developments constitute the basis of the study of the electrophoretic transport of colloidal particles, their polarisation interaction in an electric field (electrocoagulation), and electrochemical coagulation in the diffusion layer, which determine the mechanism of the formation of polymer coatings. Colloidal-chemical factors determine the possibility of regulating the conditions in the electrochemical reduction of ions and the electrocrystallisation of colloidal metal deposits.

This review considers the main principles and the mechanism of the formation of metallopolymer coatings and materials. The development of this branch of electrotechnology involves the solution of a number of problems in colloid chemistry, electrochemistry, and the physical chemistry of filled polymers. They include (1) the study of the mechanism of the formation of the charge on polymer particles and the possibility of regulating it (in connection with the electrophoretic transport and aggregation of particles on the electrode), (2) the study of the electrophoretic deposition of dispersions, especially the drift of the particles to the electrode, and of

the mechanism of the coagulation of polymer dispersions under the influence of the electric field and products of electrochemical reactions in the diffusion layer, (3) the study of the influence of the electrophoretic deposition of colloids on the polarisation of the electrode and the electrocrystallisation of the metal, (4) the study of the electrode reactions determining the deposition of metals and polymers on electrodes with a metallopolymer coating, and (5) the study of the interaction of polymers and metals in joint electrodeposition and heat treatment.

II. ELECTROPHORETIC DEPOSITION OF POLYMER DISPERSIONS

The electrophoretic deposition of dispersions includes the following stages: the charging of the polymer particles; their movement to the electrode accompanied by their aggregation in space; the coagulation of the particles in the region near the electrode; the heterocoagulation and adhesion of the particles to the electrode.

The electrodeposition of polymers from solutions involves, firstly, the movement to the electrode of macroions (polyelectrolytes) or ionised aggregates and, secondly, loss of solubility by them in the region near the cathode on interaction with precipitant ions.[3,9] Presumably, the polymer segregation process subsequently proceeds analogously to the way that this occurs in electrophoresis, including coagulation, heterocoagulation on the electrode, and the formation of a deposit which is a colloidal structure consisting of globular particles. It is important to note that both processes involving deposition from aqueous media are controlled by electrode reactions in which water is decomposed and the electrodes ionised, as a result of which an electrolyte concentration gradient is created, which is responsible for the segregation of the polymer in an insoluble form and its subsequent coagulation.

Three main mechanisms of coagulation in the electrodeposition of dispersions and the electro-osmotic compaction of the deposits formed are known at the present time: (1) electrochemical; (2) electrocoagulation; and (3) accumulative. The role of each depends on the specific physicochemical properties of the dispersed systems in the layer near the electrode and the parameters of the external electric field.

1. The Electrocoagulation Mechanism

The formation of a deposit on the electrode in an electric field is associated with the stability of dispersed systems characterised by the potential energy curves for the interaction between the particles or, in other words, by the balance of the forces acting between them. A quantitative description of the interaction of dispersed particles based on the general concept of the wedging pressure has been proposed.[24,25] Under certain conditions, two minima can appear on the overall potential energy curve for the interaction (for large and small distances between the particles) and a maximum can appear for intermediate distances. This character of the curve can be explained by the fact that the molecular and ionic-electrostatic interaction forces depend in different ways on the distance between the macroparticles: the former decrease in accordance with a power law and the latter decrease exponentially. The depth of the nearest potential well $U_{\min} \gg kT$ is determined by the degree of compensation of the molecular attractive forces by the Born repulsive forces.[26]

Coagulation, corresponding to a deep first minimum, leads to the formation of aggregates at the surface of the particle, which do not decompose after the external electric field has been switched off (irreversible coagulation). When a sufficiently high potential barrier exists, the electric field is responsible for the fixation of the particles, which corresponds to the second minimum on the potential curve. Depending on the depth of this minimum, the aggregation of the particles is reversible or irreversible.[4,27-29]

It has been shown[30] that the formation of the electrophoretic coating in the electric field is determined by the action of ionic-electrostatic forces, the repulsive forces of the non-overlapping non-deformed double layers, the dispersion attractive forces, and the dipole–dipole forces, which are manifested over distances $S = 2 + h/a$, where a is the radius of the spherical particle and h the distance between the particles. If the distances are less than a, the forces are converted into the more powerful multipolar forces due to repeated mutual polarisation, manifested solely over short distances. Allowance for the polarisation forces leads to the appearance (or deepening) of a second minimum, the depth and the coordinate of which are determined, other conditions being equal, by the strength of the active electric field.

For not unduly strong fields, where the deformation of the weakly overlapping double layers can be neglected, the total energy of the interaction between the particles is

$$U_e = U_i + U_m + U_E . \qquad (1)$$

A formula for the calculation of ionic-electrostatic repulsion U_i of the particles corresponding to arbitrary values of ϕ_δ for $\varkappa a \gg 1$ and $\varkappa a \cong \varkappa h \gg 1$ has been proposed[31] (a is the particle radius, $\varkappa$ the Debye shielding radius, and ϕ_δ the Stern potential). The molecular attraction energy U_m, expressed as a function of the distance between the particles, can be determined from the Hamaker formula for spherical particles.[32] The dipole–dipole attraction U_E can be calculated from the formula proposed by Estrela-Lopez et al.[30] The uniformity of the coating is determined by the uniformity of the packing of the particles in the film. More favourable conditions for this are created in reversible coagulation corresponding to the second minimum on the energy curve, whereupon the particles retain their ability to migrate in the film as a result of the interaction with the field and with the nearest neighbours and to fill uniformly all the cavities.[33,34] It has been shown[30] that the role of the dipolar forces increases with increasing size of the particles of the disperse phase. As the electric field strength increases, the depth of the second minimum also becomes more marked and the distance between the particle diminishes. Thus the increase in the electric field strength leads to the growth of the cohesive forces and to the compaction of the structure of the deposits.

Calculation of the potential curve for the interaction of the particles of a dielectric, semiconductors, and metals in the absence of a field and in an electric field showed that the increment in the energy of the attraction of the polarised particles under the influence of the field promotes the complete disappearance of the potential barrier.[11] At the same time, for a sufficiently high barrier, the imposition of the electric field induces the appearance of deep secondary minima responsible for further aggregation of the particles and the formation of the deposit. With increase in the electric field strength, the depth of the second minimum likewise rises.[35] In the study of the processes involving the formation of an electrophoretic coating in the region of the second minimum, it is necessary to take into account the

collective interaction of the particles in a limited or constrained volume.[4,36] Such conditions are satisfied by the layer near the electrode with an increased concentration of the disperse phase, where the particles are separated by distances comparable to their radius, which increases the attractive forces between them.[37]

In order to carry out the electrophoretic deposition, it is necessary that the electric field strength and the duration of its action should be must less than certain critical values.[38] The time necessary for the occurrence of coagulation processes is called the "critical time" τ^*. The ideas concerning the critical time have been developed in a number of studies.[11,39,40] According to Us'yarov and co-workers,[27,28] in the general case τ^* is the average statistical time required for the formation of fairly large aggregates. However, the main stage determining τ^* is the formation of a strong bond between two particles. On the basis of the slow coagulation theory allowing for the change in the concentration of particles in the space near the electrode and under conditions where a doublet is formed in the remote well, τ^* can be determined:[41]

$$\tau^* = \frac{\sum^{i} \exp\left[U(\varphi)_{max}/RT\right] \Delta\varphi_i}{64\pi^2 D r^3 N_x \varkappa}, \qquad (2)$$

where r is the radius of the particle, $U(\phi)_{max}$ the potential barrier of the interaction, $\Delta\phi_i$ the specified range of values of the angle between the direction of the field and the axis of the induced dipole, D the diffusion coefficient of the particles, and N_x the concentration of the particles in the layer near the electrode.

Together with the critical time, an important characteristic of the electrodeposition process is the "critical electric field strength" E^*, i.e. the field strength for which the formation of the coagulation structure begins. It has been shown[41] that $\tau^* \propto E^{-2}$, i.e. E^* and τ^* are inter-related quantities which are functionally linked to the parameters of the system and the electrodeposition conditions. The determination of these quantities requires allowance for the polarisation interaction; otherwise there is a possibility of large discrepancies between the calculated and experimental values.[42] Examination of the aggregation of particles from the standpoint of slow coagulation[43] suggests that each pair of particles which have collided forms a doublet. The critical electric field can be estimated from the formula

$$E^* = \frac{4\pi\sigma_0}{\varepsilon_0}, \qquad (3)$$

where σ_0 is the electrical conductivity of the medium and ε_0 the dielectric constant. The aggregation of particles in the layer near the electrode is accelerated not only by an increase in the electric field strength but also following an increase in the concentration of the suspension.[41]

The question of the interaction of the particle with the surface of the electrode is no less important. It follows from the heterocoagulation theory that the optimum deposition conditions are ensured for unlike charges of the electrode and the particle.[44] When the signs of the charges are identical, the wedging pressure plays an appreciable role.[41] The interaction of the particle with the electrode is regarded[45–47] as the result of the attraction due to the image forces, which are dipolar in nature. A formula has been obtained according to which the dipolophoretic attraction becomes significantly greater than the electrophoretic force with decrease in the distance to the electrode surface. The attractive forces are proportional to the radius of the particle raised to the sixth power.

The role of the electrocoagulation mechanism in the formation of coatings in aqueous organic media was tested experimentally by investigating the dependence of the yield of the deposit on the polarisation of the particles of the disperse phase.[48] In the isopolarisation state, the polarisation criterion is described by the expression

$$\mathrm{Rel}_{iso} = \frac{\cosh\frac{\varphi_\delta}{2} - 1}{\varkappa a} = \frac{1}{2}. \qquad (4)$$

The electrophoretic deposition of an aerosol dispersion in isopropyl alcohol—water mixtures with an increasing water content has been investigated.[48] In the absence of dipolar interaction between the particles and the electrode, in the isopolarisation state the yield of the deposit formed via the electrocoagulation mechanism is minimal. Studies have shown that a change in the composition of the dispersion medium can serve as a fine instrument for varying the contribution of the electrocoagulation and the electrochemical mechanisms to the electrophoretic deposition of dispersions. Thus it is possible to regulate the process involving the formation of the coatings and the structure and properties of the latter.

2. The Electrochemical Mechanism

The electrochemical mechanism presupposes the formation, in the zone near the electrode, of an excess electrolyte concentration front which spreads into the surrounding space; these ideas date back to two studies.[38,49] In the above mechanism the critical time τ^* is interpreted as the time necessary to create the threshold electrolyte concentration at which the stability of the system decreases and the particles coagulate on the electrode in conformity with the Deryagin–Landau–Verwey–Overbeek (DLVO) theory.[24,25,50,51] The excess electrolyte concentration in the diffusion layer at the electrode c_{el} tends to the initial concentration c_0 under conditions such that the concentration of ions changes as a result of diffusion and electromigration:[49]

$$c_{el} \to c_0 = \frac{2}{\pi^{1/2}} \frac{It_m}{SF} \left(\frac{\tau}{D}\right)^{1/2}, \qquad (5)$$

where I is the current, t_m the transport number of the ions M^+, D the diffusion coefficient of the ion pair M^+OH^-, S the electrode surface area, F the Faraday, and τ the deposition time.

The formula for τ^* can be represented in the form

$$\tau^* = pI^{-2} = qU^{-2}\sigma^{-2} \qquad (6)$$

where p and q are constants, U is the potential, and σ the conductivity of the suspension. Thus the critical time is inversely proportional to the square of the potential of the electrodes and to the conductivity of the suspensions. The experimental confirmation of these relations is one of the proofs of the validity of the theory considered. The DLVO theory, developed for systems with a conducting dispersion medium, can also be used to calculate parameters which determine the stability of dispersions in the region near the electrode in a weakly conducting non-polar dispersion medium.[38,49]

The ideas concerning the role of the electrochemical mechanism of the coagulation of particles in the formation of a deposit were developed further in other investigations.[2,52,53] Analysis of the experimental and theoretical data shows that the electrophoretic deposit is formed in two stages and that the process includes the transition from reversible to irreversible coagulation and also an increase in the concentration of the

polymer and electrolyte species in the diffusion layer near the electrode. Electrochemical coagulation can therefore take place via a concentration mechanism (determined by the compression of the electrical double layer) and a neutralisation mechanism (associated with a decrease in the charge).

The degree of reversibility of the coagulation and hence the thickness and strength of the deposit are determined by the spatial-temporal distribution of the coagulating ions in the zone near the electrodes. The relations illustrated in Fig. 1 give an idea of the processes involving the formation of deposits from the polymer particles.[53] The factor determining the kinetics of the formation of the deposit is the change in the overall concentration of the coagulating ions, in the given instance hydroxide ions. With increase in the electrolyte content in the diffusion layer (Fig. 1*a*, curve *1'*), the dimensionless electrokinetic potential $\tilde{\zeta} = (F/RT)\zeta$ decreases (curve *1*) owing to the compression of the double layer.

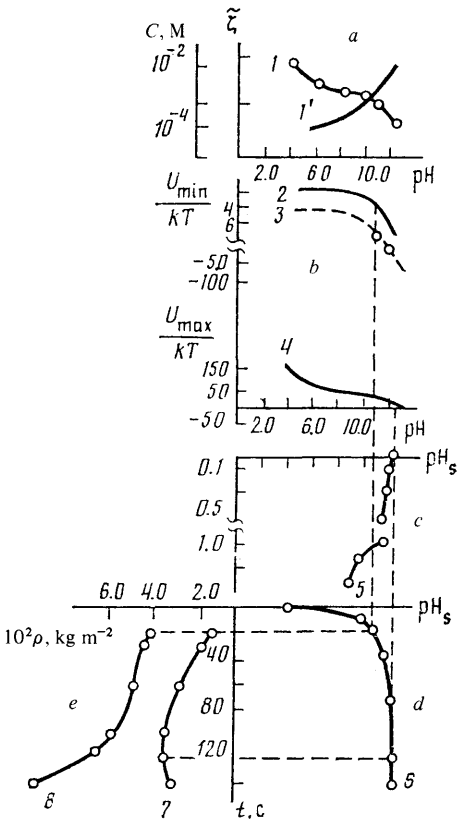


Figure 1. *a*) Dependence of the electrokinetic potential (ζ) of the particles of an epoxide oligomer (curve *1*) and of the electrolyte concentration (curve *1'*) on the pH; *b*) dependence of the energy of the interaction of a particle doublet under the usual conditions (curve *2*) and under constrained volume conditions (curve *3*) and of the potential barrier preventing aggregation (curve *4*) on the pH; *c*) variation of the pH of the dispersion in the layer near the electrode with the distance *l* to the electrode 40 s after the onset of deposition; *d*) variation of the pH in the layer near the electrode with deposition time; *e*) dependence of the yield of the deposit (ρ) formed as a result of irreversible aggregation only (curve *7*) and as a result of the joint reversible and irreversible aggregation (curve *8*) on deposition time.[53]

The decrease in the potential ζ in coagulation of the concentration type deepens the remote potential well (Fig. 1*b*, curves *2* and *3*) and decreases the potential barrier (curve *4*). The probability of the long-range (reversible) and short-range (irreversible) coagulation of the particles increases correspondingly. The first stage in the deposition process is intense reversible coagulation. After 20 s, the pH increases from 3.8 to 11.0 near the electrode (Fig. 1) to 8.0 at a distance of 0.3 mm from the electrode. The subsequent increase in pH is determined by the balance between the formation of OH^- ions in electrolysis and their consumption in diffusion and migration processes. At a distance $l = 0.5$ mm from the electrode, the pH has constant values, while in the presence of polymers the pH decreases appreciably (Fig. 1*c*).

At pH 11.0 the ζ potential is 0.9 (Fig. 1*a*, curve *1*) and the potential barrier U_{max} is still fairly high (Fig. 1*b*, curve *4*). However, the binding energy of the particles U_{min}, determined by the depth of the remote potential well recalculated to give the number of nearest particles, is entirely sufficient for their mutual fixation (Fig. 1*b*, curve *3*). The fraction of the reversible deposit exceeds appreciably that of the irreversible deposit (Fig. 1*e*). The deposit is readily peptised after the removal of the field.

With increase in the electrodeposition time and with increase in pH at the electrode surface from 11.0 to 12.2, the ζ potential falls to 0.45 (Fig. 1*a*, curve *1*). This threshold value of the ζ potential corresponds to the onset of irreversible coagulation. The potential barrier preventing the coagulation of particles then disappears (Fig. 1*b*, curve *4*). The yield of the irreversibly coagulated deposit at high pH becomes a maximum (Figs. 1*c*, 1*d*, and 1*e*). The overall yield of the deposit also increases (Fig. 1*e*, curve *8*); with increase in pH, the reversible coagulation begins at a certain distance from the electrode and the deposit is partly formed from aggregates weakly bound to the electrode. The amount of the irreversibly coagulated deposit then falls.

Analysis of systems with the neutralisation type of electrochemical coagulation showed that their principal feature is a large contribution by irreversible coagulation to the deposit formation process.[54] The deposition from such dispersions proceeds almost without a critical time.

Systems with the concentration type of electrochemical coagulation are more plastic in the sense that there is a possibility of controlling the kinetics of the deposit formation on the electrode, but the process is in this case longer and the amount of deposit formed is smaller than in systems of the neutralisation type. The concentration systems are most suitable for the preparation of high quality electrophoretic deposits. The electrochemical purification of the liquid is best performed by the electrochemical coagulation of the neutralisation type.

3. The Accumulative Mechanism

The electrophoretic deposit is formed via the accumulative mechanism as a result of the coagulation of particles at the electrode under the influence of the forces developed by the external electric field and the molecular attraction forces. It has been suggested[55] that the process involving the preparation of a deposit by the electrophoretic method is analogous to the sedimentation of particles in the gravitational field. The role of the electric field is to supply particles to the electrode and to compact the deposit on the electrode surface. According to the accumulative theory,[55] a distinctive feature of this mechanism is the direct proportionality of the critical deposition time τ^* to the square of the field strength and its inverse proportionality to the concentration

of particles. This mechanism makes a significant contribution to the formation of a deposit from concentrated systems and in the case of dilute dispersions it is manifested in the zone near the electrode to a greater extent the higher the content of the disperse phase under the constrained volume conditions. The principle postulates and conclusions concerning the accumulative mechanism have been described in detail.[1,55,56]

All three deposit formation mechanisms are accompanied by the electro-osmotic compaction of the deposit,[11] which is an additional factor in the formation of the coating. The electro-osmotic component must be manifested appreciably as the deposit becomes denser and its thickness increases. It alters the distribution of the concentration of the particles in the region near the electrode, which leads to the appearance of a clarified layer of dispersion medium at the upper boundary of the deposit being formed. The liquid in the layer moves upwards and entrains the dispersed particles of the suspension, some of which contribute to the growth of the electrophoretic deposit. It has been shown[57] that the electrokinetic potential calculated from the flow rate of the medium in concentrated suspensions approaches the ζ potential determined by the electro-osmotic method. Thus the formation of the electrophoretic deposit is accompanied by the electro-osmotic migration of the dispersion medium, which promotes, on the one hand, an increase in the density of the layer of suspension near the electrode and, on the other hand, it inhibits the motion of the particles, since it is directed in opposition to it. Estimation of the electro-osmotic compaction forces showed that they increase with increasing concentration of the dispersion phase.[57]

4. Cataphoretic Deposition of Polymer Dispersions

In the conclusion of this Section, we shall consider the characteristic features of the electrophoretic deposition of polymer dispersions on the cathode (for aqueous organic suspensions of epoxide and phenol-formaldehyde oligomers).[48] The character of the electrochemical coagulation—neutralisation or concentration—plays a significant role in the deposit formation process. The results of the study of the electrophoretic deposition of the epoxide oligomer via the concentration mechanism and of the phenol-formaldehyde oligomer via the neutralisation mechanism from an aqueous organic medium are presented in Table 1. Evidently there are fundamental differences in the formation of deposits via the two mechanisms.

The deposition of the epoxide oligomer begins after a critical time, amounting to 20 s, has elapsed, which is associated with the attainment in the diffusion layer of the pH necessary for coagulation (in the given instance 11.0). It is noteworthy that coatings based on the epoxide oligomer are formed in two stages: reversible and irreversible coagulation. The duration of the first stage is between 20 and 50 s and that of the second between 60 and 120 s. The two-stage nature of the deposition process is a necessary precondition for the preparation of a uniform coating, since favourable conditions for the distribution of particles over the entire area of the electrode are created in reversible aggregation. The deposit is fixed in the irreversible coagulation stage. The phenol-formaldehyde oligomer is deposited immediately without a critical time.[48] The formation of the coating is caused mainly by irreversible coagulation. A common feature of the systems investigated is the formation of a deposit within the limits of the diffusion layer. In the course of the formation of the deposit, the ratio of its components, formed as a result of the reversible and irreversible coagulation, changes with time and there is an overall tendency towards an increase in the yield of the polymer. The ratio of the reversible and irreversible aggregations makes it possible to determine the parameters of the deposition process (cathodic current density, deposition time, and field strength) for which the optimum properties of the coating are attained.

Table 1. Parameters of the processes involving the electrophoretic deposition of polymers from an aqueous organic medium via the concentration and neutralisation coagulation mechanisms.

t, s	pH_s	$10^2\rho_1$, kg m^{-2}	$10^2\rho_2$, kg m^{-2}	l, mm	δ, mm
Epoxide oligomer*					
2	6.50	0.45	0.60	0.70	0.01
5	8.60	0.80	0.96	0.80	0.016
10	9.80	1.1	1.30	0.85	0.018
20	11.00	1.50	2.00	0.90	0.025
80	11.80	3.20	1.30	1.10	0.025
140	12.20	3.00	5.80	1.10	0.055
Phenol-formaldehyde oligomer**					
2	6.15	0.41	0.11	0.40	0.010
10	8.80	0.88	0.24	0.50	0.016
30	10.70	6.20	2.60	0.85	0.055
40	10.80	6.00	3.20	0.85	0.070

Notation: t is the deposition time, pH the pH value near the electrode, ρ_1 the yield of the irreversible part of the deposit, ρ_2 the yield of the reversible part of the deposit, l the thickness of the diffusion layer, and δ the thickness of the coating.

* Concentration coagulation.
** Neutralisation coagulation.

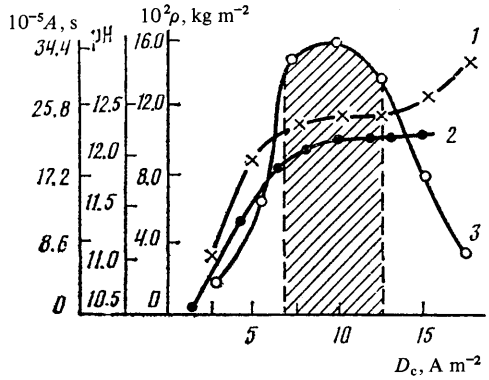


Figure 2. Dependence of the yield (ρ) of the electrophoretic deposit of an epoxide oligomer (curve *1*), of the pH of the layer near the electrode (curve *2*), and of the corrosion stability (A) of the coatings (curve *3*) on the cathodic current density.[48]

Fig. 2 presents the dependence of the yield of the deposit of the epoxide oligomer, the pH of the diffusion layer, and the corrosion stability of the coatings on the cathodic current

density. Since the electrode deposition process is an electrode reaction, I = const. is a necessary condition. The cathodic current density D_c is chosen so that it is possible to regulate the conditions in the electrochemical reactions determining the course of the coagulation processes. The increase in D_c in the initial section is accompanied by a parallel increase in the pH of the diffusion layer, the yield of the deposit, and the corrosion stability of the coatings in a chamber with 100% humidity. The increase in the amount of deposit and the pH ceases after the attainment of pH 12.2. The region D_c = 7–12 A m^{-2}, corresponding to the maximum stability of the films in the corrosion medium (shaded in Fig.2), also corresponds to the transition from reversible to irreversible coagulation (pH 12.2). The decrease in the anticorrosion stability at D_c > 12 A m^{-2} is associated with the intensification of the electrochemical reactions, the spreading to the bulk phase of the increased electrolyte concentration front, and the deposition on the electrode of the large aggregates of particles formed under these conditions. This entails the growth of the yield of the deposit and the simultaneous increase in its porosity. Thus there is a direct relation between the deposit formation conditions, the relative contributions of the reversible and irreversible coagulation, and the corrosion stability of the coatings (Fig.2 and Table 1). The methods for the preparation of composite polymer coatings with anticorrosion, protective-decorative, and electrically insulating properties have been described.[58–62]

III. ELECTRODEPOSITION OF POLYMERS AND METALS

1. The Mechanism of the Formation of Metallopolymer Deposits

The metallopolymer deposits are formed as a result of the simultaneous electrodeposition of polymer dispersions and the electrochemical segregation of the metal. The electrophoretic precipitation of the polymer deposit and the interaction of the particles of the disperse phase in the zone near the electrode play a decisive role in this process. The electrodeposition and electrocrystallisation of the metal depend in their turn on the kinetics of the formation of the polymer layer on the electrode. The structure of the metallopolymer deposit is determined by the character of the polarisation and chemisorption interactions between the polymer and metallic particles.

In this connection, we shall consider the mechanism of the formation of metallopolymer coatings from the standpoint of the influence of surfactants and polymers on the discharge of metal ions and the formation of colloid deposits. The process involving the formation of the metallopolymer deposit on the electrode begins with the formation of a polymer layer through which metal ions move to the electrode as if through a membrane. The supply of ions to the electrode surface is the rate-limiting stage. The influence of the polymer layer on the metal ion reduction process is determined by the concentration of the disperse phase, the charge on the polymer particles, their size, and the deposition conditions. The conditions governing the creation of a controllable flux of metal ions migrating to the cathode and the interaction between the particles of the segregated polymers and metals determine the composition and structure of the deposits.

The homocoagulation and heterocoagulation interactions between the polymer and metallic particles depend on the colloidal-chemical properties of the system and on the deposition conditions.[1] If the polymer particle is deposited on a metallic particle (heterocoagulation) in the formation process, then the growth of the metallic particle is greatly inhibited. In the case where the polymer particles interact mainly with one another during deposition (homocoagulation), metallic particles are formed and grow freely. The relative contributions of homocoagulation and heterocoagulation are determined by the balance between the electrophoretic (F_{ef}) and dipolophoretic (F_d) forces. When a deposit is formed from dispersions characterised by high electrokinetic potentials of the particles, low electrolyte concentrations, and the quantity Rel > 1, it is found that $F_d/F_{ef} > 1$. The active inhibition of the electrocrystallisation of the metal under these conditions makes it possible to segregrate the metal in the form of particles of highly dispersed powders uniformly distributed within the polymer. In the codeposition of particles of the epoxide oligomer and lead, the latter are produced with an irregular form and their size is 0.1–0.3 μm.[1]

In the electrodeposition of dispersions with a low ζ potential and with the parameter Rel ≪ 1, we have the ratio $F_d/F_{ef} < 1$. The structure of the deposit changes significantly in this case, since the polymer being deposited inhibits to a lesser extent the growth of metallic particles. They are needle-shaped and their size is up to 2–5 μm. Under these conditions, there is a possibility of obtaining coatings with a high metal content (up to 90–96%) and a thickness up to 100 μm, since the metal dendrites formed are conducting.

The ideas described above concerning homocoagulation and heterocoagulation can explain the results obtained in the experimental study of the codeposition of polymers and metals. A general tendency is an increase in the yield of the deposit with increasing concentration of the disperse phase and charge on the particles and a decrease in the metal content of the latter. An increase in the electrolyte concentration naturally diminishes the potential and also increases the parameter a and decreases Rel. Dipolophoresis and electrophoresis promote the homocoagulation of the polymer particles. The growth of metallic particles is not blocked, which increases the metal content in the deposit.

With increase in the concentration of polymer particles and their charge, the simultaneous occurrence of dipolophoresis and electrophoresis promotes the interaction of the polymer and metallic particles, i.e. heterocoagulation. The effect, involving the blocking of the electrode surface and of the metallic particles by the polymer particles, leads to the appearance of a new form of overpotential, which we have called the electrophoretic overpotential. The electrophoretic overpotential influences the electrocrystallisation of the metal as a rule to a much greater extent than the adsorption of a surfactant on the electrode.[18,63,64–67]

Fig.3 illustrates the polarisation curves for a copper electrode in 0.032 M $Cu(HCOO)_2$ solution containing a biquaternary ammonium compound and a dispersion of the organosilicon oligomer. The joint action of the surfactant and the polymer results in the discharge of the copper ions under the conditions of appreciable cathodic polarisation. At low current densities, a shift of the polarisation curves towards negative potentials is already observed: by 220 mV in the presence of the surfactant and by 480 mV in the presence of the polymers. When the quaternary ammonium compound (Fig.3, curve *2*) and the disperse phase (curves *3–5*) are introduced, the current maxima on the curves are reduced and sections appear along which the current depends little on the potential. This indicates an increase in the activation energy necessary for the penetration of metal ions through the polymer layer and their discharge on the electrode.

The electrophoretic polarisation depends directly on the colloidal chemical properties of the dispersions deposited, which determine the relative contributions of homocoagulation and heterocoagulation in the deposit. Table 2 presents the most typical data characterising the codeposition of dispersions and colloidal metals. The electrophoretic polarisation increases with increasing ζ potential of the polymer particles. The increase in the electrokinetic potential increases in its turn Rel and heterocoagulation.[18] For example, the increase in the ζ potential of the epoxide oligomer particles from +36.2 mV to +115.5 mV corresponds to a change in Rel from 0.12 to 0.87.

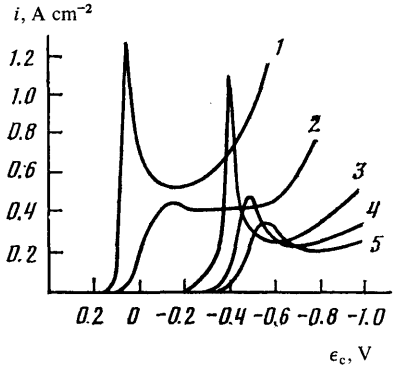


Figure 3. Cathodic polarisation curves for a copper electrode: *1*) in 0.032 M $Cu(HCOO)_2$ solution; *2*) ditto with added 0.5 mm surfactant; *3*) ditto with added disperse phase [*3*) 0.125%; *4*) 0.25%; *5*) 0.50%][83] (*i* is the current density and ε_c the potential).

Table 2. The influence of the ζ potential of the epoxide oligomer particles and their concentration on the polarisation of the electrode in codeposition with lead [electrolyte 0.005 M $Pb(HCOO)_2$].[19,68]

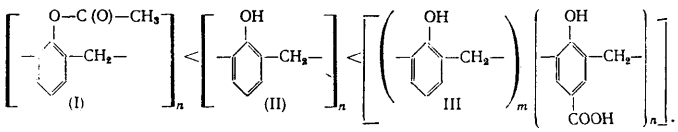
ζ potential, mV	Shift of polarisation curves, V	Concentration of disperse phase, wt.%	Shift of polarisation curves, V	Yield of polymer component, mg cm^{-2}
−36.2	0.8	0	0.1	0
+43.7	0.9	0.06	0.35	6.4
+54.0	1.1	0.31	1.4	8.3
+84.8	1.3	0.94	1.9	10.1
+115.5	1.6	2.25	2.6	12.8
		2.6	3.3	12.1

The next factor determining the effectiveness of the increase in the overpotential of the segregation of metals in the formation of the metallopolymer deposit is the increase in the concentration of the disperse phase in the electrolyte solution.[68] Thus the increase in the epoxide oligomer concentration increases the polymer content in the metallopolymer deposit and leads to the growth of the lead reduction overpotential, which is indicated by the shift of the polarisation curves towards negative potentials by 3 V (Table 2); under these conditions the metal is produced in a highly dispersed state.

The effective activation energy for the discharge of lead ions increases from 28 to 74 kJ mol^{-1} with increase in the concentration of the disperse phase from 2.5 to 5 wt.%.[18] This is accompanied by a decrease in the size of the metal particles from 2–3 μm to 0.2–0.5 μm and a change in the crystal structure; the size of the blocks of the mosaic falls from 1590 to 200 Å.

Not only the polarisatio. interaction between the polymer and metallic particles but also the chemisorption interaction processes between them play an important role in the establishment of the conditions governing the polarisation of the electrode. In the process involving joint segregation on the electrode, the epoxide oligomers interact with the surface of the lead particles with opening of the epoxide rings.[15] For example, a 2.2 V cathodic shift of the polarisation curves has been observed for epoxide oligomers containing 2.2% of epoxide groups, while in the presence of an epoxide content of 21.8% the shift was by 3.4 V other conditions being equal. The displacement of the epoxide groups in the oligomer chain by hydroxy-groups reduces this effect to 0.7–0.9 V.

Analogous results have been obtained in the electrodeposition of dispersions of phenol-formaldehyde oligomers and zinc.[65,66] When oligomers with hydroxy- and carboxy-groups and oligomers in the chains of which these groups have been replaced by ester moieties are used, the zinc electrocrystallisation overpotential increases in the sequence



The chemisorption interaction between the polymer and metallopolymer particles has two important consequences: firstly, together with the increase in the ζ potential of the polymer particles and in their concentration, this is a fine instrument for regulating the degree of dispersion and the structure of cathodic metal deposits and, secondly, as will be shown below, the formation of surface compounds and the shielding of such surfaces of metallic particles constitute the basis of corrosion stability of metallopolymer coatings.[1,56]

An increase in polarisation and hence a decrease in the metallic particle size have been noted in the codeposition of zinc with phenolformaldehyde oligomers of type (III) with increase in their content of carboxy-groups from 2 to 16%.[67] The increase in polarisation indicates a significant change in the rates of both principal stages of the metal segregation process: the penetration of metal ions to the electrode and their discharge.

The change in the polarisation of the electrode is caused by the joint influence of the biquaternary ammonium salts and polymer particles on the parameters of the electrical double layer and the diffusion layer at the electrode. The adsorption of surfactants plays an important role in the initial period of the formation of the metallopolymer deposit, influencing the electrical double layer at the electrode surface.[64] As a rule, the formation of the adsorption layer is accompanied by a decrease in the exchange current and an increase in the surface coverage, which reaches the limiting value of 0.87 at a surfactant concentration of 2 M.[64]

Thus examination of the data obtained permits the conclusion that the characteristic feature of the segregation of the metal in the formation of the metallopolymer deposit consists in the fact that it occurs under the conditions of very pronounced adsorption and electrophoretic concentration polarisation. The rate-limiting stage of the process becomes the diffusion of metal ions M^{2+} through the polymer layer.

The diffusion boundary layer is localised within the deposit. A steady state reaction is established after the attainment of a constant thickness of the latter. Up to this instant, the process is non-stationary, the thickness of the diffusion layer increases with time, and the balance between the rate of the electrochemical discharge of metal ions and the rate of their supply and also between the concentrations of the discharging ions and ions diffusing into the solution is disturbed. The electrochemical reaction proceeds in accordance with the general laws of the diffusion kinetics of heterogeneous processes in solutions.[71,72] The thickness of the diffusion layer reaches ~500 μm under the conditions of the electrophoretic deposition of polymers and the electrochemical segregation of the metal, which agrees with data obtained in an unstirred solution[73] and is close to the values which have been obtained in the study of processes involving the electrophoretic deposition of polymers (Fig.1). The principal characteristic feature of the formation of such a layer in a combined process consists, in contrast to the processes involving the segregation of pure metals, in slow diffusion into the bulk phase and an appreciable accumulation of OH^- ions in the layer near the electrode.

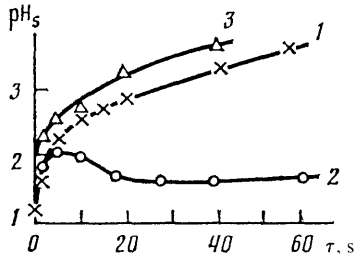


Figure 4. Dependence of pH_S on the electrodeposition time (τ) for a dispersion of a phenol-formaldehyde oligomer (curve *1*), lead (curve *2*), and the metallopolymer deposit based on them (curve *3*).[74]

The principal differences between the formation of the diffusion layer on deposition of metals, polymers, and metallopolymers are illustrated in Fig.4, characterising the variation of the pH in the layer near the electrode (pH_S) as a function of the process time in the codeposition of dispersions of phenol-formaldehyde oligomers and lead from solutions of lead sulphamate.[74] Studies of the variation of the pH of the layer near the electrode (pH_S) showed that the formation of a polymer film, which prevents the diffusion of OH^- ions into the bulk of the solution, leads to an increase in the pH of the diffusion layer compared with the segregation of the pure metal (without the polymer), which retards the onset of the stationary state. Analogous results have been obtained in the deposition of other resins, including the aminoformaldehyde resin.[56] An increase in pH_S leads to the segregation of metallic deposits with different phase compositions and the formation of hydrates and basic salts.[1,18,74]

The character of the diffusion processes and hence the mechanism of the formation of metallopolymer deposits are determined mainly by the relative contributions of the electrophoretic and electrochemical depositions. A transition from metallopolymer deposits to composite electrochemical coatings with a high metal content can be achieved by regulating them by varying the concentration of the disperse phase, the charge on the particles, and the concentration of the electrolyte. In the first case, the polymer is deposited preferentially: the rate of its electrophoretic deposition exceeds the rate of the electrochemical segregation of the metal.[75] Then the parameter A, characterising the ratio of the segregated polymer and metal, assumes the value $A \leqslant 0.25$. This corresponds to the conditions for electrodeposition from dilute electrolytes and to increased electrokinetic potentials of the particles in the dispersions and their concentrations (mechanism I). By varying these parameters, it is possible to equalise the rates of electrodeposition of polymers and metals and to obtain deposits of a constant composition, with respect to thickness, and a uniform structure. If the rate of segregation of the metal exceeds the rate of deposition of the polymer, composite coatings are formed, consisting of a metallic matrix in which the polymer particles are distributed (mechanism II). The presence of a kinetic potential of the polymer particles in concentrated electrolyte solutions indicates the important role of electrophoretic transport of the particles of the disperse phase in the formation of metallopolymer electrochemical coatings via mechanism II.[76,77]

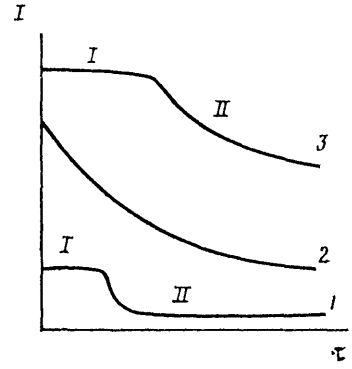


Figure 5. Schematic illustration of the dependence of the current on the time required for the deposition of polymers (curve *1*) and metallopolymer deposits from dilute (curve *2*) and concentrated (curve *3*) electrolytes.

The differences between these two processes, the first of which is determined by diffusional kinetics and the second by electrochemical kinetics, are revealed when the dependences of the current I on the deposit formation process time are compared (Fig.5). The joint deposition of the polymer and the metal via mechanism I (curve *2*) is characterised by the absence of a critical time, which is the case in the electrophoretic deposition of the polymer (curve *1*) and by an appreciable decrease in the current. The decrease in τ^* is promoted by an increase in the electrolyte concentration (OH^-) even in the first seconds as a result of electrode reactions and the rapid segregation of the metallic deposit. The sharp decrease in the current can be explained by its proportionality to $\tau^{1/2}$, which is associated with the shielding effect of the polymer deposit and with the decrease in the diffusion of M^+ ions through the polymer layer formed.

The presence of a horizontal section on the curve in the codeposition of metals and polymers from concentrated electrolytes (Fig.5, curve *3*) is associated with the preferential

segregation of the metal. The extent of the first horizontal section is limited by the time during which the composition and conductivity of the deposit remain constant. The conditions under which the resistance of the film is independent of time in the initial deposition stage, which ultimately determines that the current is independent of time, have been estimated.[75] In the deposition process, these conditions break down and, after a certain time interval, the deposit is formed under conditions where $I \propto \tau^{1/2}$, in conformity with mechanism *I*. These ideas have been confirmed by data obtained from layer-by-layer analysis.[74] The greatest metal content in the metallopolymer deposits obtained in the deposition of the phenol-formaldehyde oligomer from concentrated zinc sulphate solutions has been detected in the lower layers, the upper layers being enriched in the oligomer (Table 3).

Table 3. Results of the layer-by-layer chemical analysis of metallopolymer coatings.[74]

Coating deposition time, s	5	10	17	25	30
Thickness of coating, μm	4	6—7	10—12	14—16	20—22
Zinc content, wt.%	92	87	82	78	69

The occurrence of the conditions for diffusional kinetics in the formation of metallopolymer coatings via mechanism I follows from the estimation of the diffusion of metal ions in the deposit formation process from the equation for nonstationary diffusion for planar electrodes.[75] Here it was assumed that (1) the thickness and mass of the deposit are limited by the conditions for adequate ionic conductivity in the pores within the deposit, i.e. by the presence of metal ions in a polar dispersion medium, (2) the main bulk of the ions are supplied to the electrode surface through the polymer layer via diffusion, (3) the rate of deposition of the polymer exceeds the rate of segregation of the metal ($A \leq 0.25$), and (4) since diffusion takes place in a porous body, i.e. is independent of the migration of the dispersion medium, convective diffusion is ruled out.

The boundary conditions are determined by the fact that, after a certain time has elapsed, the concentration of ions on the electrode surface becomes zero because their diffusion through a film of large thickness is impossible. The film is formed in the presence of M^+ ions being discharged simultaneously with the deposition of the polymer.

For thin films under the conditions of long deposition times, the relation between the film thickness and the deposition time is given by the equation[7]

$$l = \left(\frac{2Dc_0\tau}{M}\right)^{1/2}, \qquad (7)$$

where *M* is the concentration of metal ions within the moist film, c_0 their concentration at the electrode surface, and *D* the diffusion coefficient of the ions. This relation has been confirmed experimentally in a study of the codeposition of an epoxide oligomer with lead.[75] The thickness of the deposit and the Faraday current are described by $l \propto \tau^{1/2}$ and $I \propto \tau^{1/2}$ respectively.

In the electrochemical reduction of metals in polymer dispersions stabilised by surfactants, the conditions for the transport not only of ions but also of polymer particles, i.e. the ζ potential, change. The introduction of small amounts of polyvalent electrolytes (10^{-5}—10^{-4} M) into the polymer dispersions stabilised by added surfactants increases the electrokinetic potential of the polymer particles as a result of the additional adsorption of the codeposited cations M^{2+}.[78] This possibility has been justified theoretically in a study[79] where it was shown that the degree of sorption of the codeposited ions is determined by the product $z\phi_\delta$ (where *z* is the valence of the ion) and diminishes sharply for $\overline{\phi}_\delta > 3$—4 as a result of the enhancement of the electrostatic repulsion. The sharp decrease in the ζ potential of the particles and in the stability of the system as regards aggregation occur for electrolyte concentrations 10^{-3}—10^{-2} M. Furthermore, the introduction of electrolytes into polymer dispersions, stabilised by surfactants, can promote an increase in the electrokinetic potential of the particles as a result of the additional adsorption of the surfactant on their surface and the compaction of the adsorption layer.[80—82] As a rule, with increase in the electrolyte concentrations, the ζ potentials pass through a maximum. The characteristic features of ion transport under these conditions are associated with the fact that the particles of the disperse phase behave as ion carriers, which makes a definite contribution to their diffusion to the electrode. The efficiency of the ion transport is determined by the magnitude and sign of the charge on the particles (ϕ_δ) and by the degree of adsorption of the surfactant.

Table 4. Dependence of the diffusion coefficient *D*, the thickness of the diffusion layer δ, and the thickness of the coating *l* on the electrolyte composition in the formation of a metallopolymer coating based on an organosilicon oligomer and copper.[63,64]

Parameter	Copper formate	Copper formate + 0.5% of oligomer dispersion	Copper formate + 0.5% of oligomer dispersion + surfactant at different concentrations, mM			
			0.13	0.50	1.00	3.00
$10^6 D$, $cm^2 s^{-1}$	1.62	2.37	1.90	1.53	1.42	1.12
$10^2 \delta$, cm	0.326	0.457	0.366	0.295	0.274	0.216
$10^2 l$, cm	—	—	0.34	0.28	0.26	0.22
$10^3 i_d \tau^{1/2}$	14.5	16.8	15	13.5	13.0	11.5

The estimation of the diffusion coefficients from Sand's equation, which is valid for linear semi-infinite diffusion,[83] showed that the introduction of particles of an organosilicon oligomer increases the diffusion coefficient of the Cu^{2+} ions (Table 4). The results obtained suggest that this effect is associated with the transport of ions by polymer particles. With increase in the surfactant concentration and hence in the positive ζ potential of the particles, the effect involving an increase in the diffusion coefficient of the Cu^{2+} ions disappears. Apparently a phenomenon somewhat similar to that of micellar catalysis, described in the literature,[84] takes place here, but, instead of surfactant micelles, the ion carriers are polar particles stabilised by such micelles. When the system contains ionogenic surfactants and cations, the charge on the particle is generated as a result of the competitive adsorption of both types of species.

The introduction of biquaternary ammonium compounds decreases the degree of adsorption of the cations on the surface of the particles.[64] With increase in the surfactant content and hence in the ζ potential, the additional sorption of the codeposited cations becomes impossible, which decreases the diffusion coefficient by a factor of two (Table 4). The

limiting diffusion current i_d changes analogously. Evidently there is a correlation between the diffusion coefficient D and the thickness of the diffusion layer δ. Comparison of the values of δ with the thickness of the coatings l shows that the coatings are formed within the limits of the diffusion layer.

The steady increase in the diffusion of the ions M^{2+} entails a decrease in the potential at which the metal is segregated at low concentrations of the disperse phase and an acceleration of the deposit formation process.[85,86] Apart from the intensification of ion transport to the electrode by virtue of the involvement of the polymeric carriers in the process, this phenomenon can be accounted for by the enhancement of the diffusion under the conditions of the simultaneous segregation of the metal and polymer particles. The formation of a three-dimensional-network of dielectric particles can lead to the deformation of the electric field strength lines in the interelectrode space and hence to an intensification of the field in the gap between the particles.

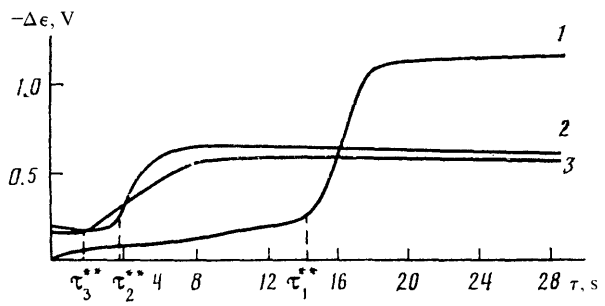


Figure 6. Time variation of the potential of a copper electrode (galvanostatic conditions) in 0.032 M $Cu(HCOO)_2$ solution containing 1% of the disperse phase and also different amounts of a surfactant [*1*) 0%; *2*) 0.75%; *3*) 2%] (D_c = 8.9 A m^{-2} is the cathodic current density).

Yet another important aspect of the mechanism of the joint deposition of polymer and metal dispersions is noteworthy. It consists in the fact that the presence of polymer particles in the diffusion layer promotes, like surfactants, a change in the electrode potential and hence in the energy parameters of the metal segregation process. In the electrophoretic-electrochemical codeposition of an organosilicon oligomer and copper in the presence of an uncharged oligomer dispersion, the electrode potential shifts appreciably towards negative values after the transient time has elapsed.[63] In the codeposition of copper with dispersions whose particles have a high ζ potential, the electrode potential diminish by a factor of 2–3 with increase in the polymer concentration (Fig. 6, curves *1* and *3*). The electrode reactions begin at higher potentials of the cathode and require an appreciable polarisation, the contributions of its individual components changing in different stages of the process. At a low current density, where the M^{2+} ions are reduced at constant (or nearly constant) potentials, the rate of the electrochemical reaction is apparently lower than the rate of diffusion of ions to the electrode surface. An appreciable overpotential, due to charge transfer, is observed. The study of the temperature dependence of the rate of the electrochemical reaction at different current densities showed that the overpotential associated with the formation of a new phase also makes a significant contribution.[64]

The nature of the overpotential and the possibility of regulating it throughout the deposit formation process determine the structure of the layer of the deposited material. At current densities close to or exceeding the limiting values, copper is deposited on the cathode in the form of a dense layer in the course of a short period equal to the transient time τ^{**}, which, as can be seen from Fig. 6, is appreciably reduced with increase in the charge on the polymer particles (τ_1^{**}, τ_2^{**}, and τ_3^{**} respectively). After the time τ^{**} has elapsed, the concentration of the discharging ions in the region near the cathode falls, the potential shifts towards more negative values, and copper is subsequently deposited in a non-compact form.

Thus, by altering the concentration of the particles of the disperse phase and their charge, it is possible to regulate the parameters of the diffusion layer and hence the reduction of the metal ions. It becomes possible to carry out the electrocrystallisation process under conditions of increased activated inhibition and high polarisation.

In connection with the formation of metallopolymer coatings via mechanism II, the phenomenon of the electrophoretic mobility of polymer particles in concentrated electrolyte solutions merits a separate discussion. The presence of the electrokinetic potential in dispersions with a high electrolyte content requires a new approach to the treatment of the mechanism of the formation of the electrical double layer. At the present time, there exist several hypotheses.[76,87] In the presence of ionogenic surfactants, the increase in the electrophoretic mobility of particles with increase in the electrolyte concentration can be associated, as stated above, with increase in the surface charge density as a consequence of the adsorption of the surfactant.[18,81,88] Presumably the potential around a charged particle in concentrated electrolyte solutions will oscillate and its dependence on concentration will therefore have a complex non-monotonic character.

On the basis of ideas concerning the disruption of the solvate layer by electrolytes, presumably an increase in the electrolyte concentration entails a shift of the slip plane, separating the stationary and mobile parts of the double layer, towards the interface.[89] It has been suggested that the solvate layer is disrupted faster with increasing electrolyte concentrations than the diffuse layer is compressed.

Allowance for the different solvent powers of the solvate layer in relation to anions and cations demonstrated the possibility of increasing the potential of the solvated particles in concentrated electrolyte solutions and the appearance of an electrostatic stability factor of a new type.[90] Studies on these lines are important both for the development of a technology for the deposition of coatings and for the solution of the problem of the stability and generation of the charge on dispersed systems in concentrated electrolyte solutions.

IV. THE STRUCTURE AND PROPERTIES OF METALLOPOLYMER COATINGS

The extensive possibilities for regulating the composition and structure and hence also the properties of metallopolymers permit their use as effective anticorrosion, antifriction, and electrically conducting coatings. The advantages of anticorrosion metallopolymer coatings over polymer coatings arise from the fact that the protective properties of polymers are supplemented by the protective or inhibiting effect of the corresponding metals. The strength and stability of the metallopolymer coatings are as a rule higher than those of

the polymer coatings. Two-layer protective-decorative coatings can be obtained from electrically conducting metallopolymer compositions by electrodeposition.

Metallopolymer coatings are multicomponent systems containing a mixture of oligomers and polymers together with colloidal particles of metals and alloys. Their electrophoretic-electrochemical codeposition on the electrode is in essence the first stage in the formation of the coating. The properties of the composite metallopolymer material formed under these conditions are determined to a large extent by its subsequent hardening at elevated temperatures and mainly by the interactions between the polymeric components and the surface of the metal particles. The segregation of the metal particles, which have an active surface, together with the polymer promotes an increase in the fraction of chemisorption bonds in the system. The nature of the polymer and the type and number of functional groups play the main role in this process.

As a result of the thermal interaction of the oligomers and polymers with the surfaces of colloidal metallic particles, various surface compounds with bonds of different types are produced.[15,16] Ionic bonds (polysulphide) or M–O–C bonds of the covalent type (epoxide and polyester oligomers, polyethylhydrosiloxane) are formed in polymers containing groups with locally concentrated charges. Polymers containing tervalent nitrogen, for example, acrylic oligomers [sic], are capable of interacting with the atoms on the surface of the metallic particles with formation of coordinate bonds. If the polymers contain ether, ester, and hydroxy-groups [polyether and phenol-formaldehyde oligomers and poly(vinyl acetate)], then there is a possibility of their interaction with the surface to form dipole–dipole, ion–dipole, and hydrogen bonds.

Studies on processes involving the formation of metallopolymer coatings from mixtures of oligomers and oligomer–polymer mixtures showed that in this case the compatibility and the interaction of the polymeric components play an important role.[15] The most satisfactory physicochemical properties of the coatings are then attained for the ratio of the components which corresponds to the range of their compatibility or the formation of graft copolymers in the system.

The study of the structure and properties of metallopolymer coatings is part of the general problem of the formation of composite polymeric materials containing fillers of different kinds.[15,16,91] The mechanism of the action of fillers consists in the general case in the fact that in their presence adsorption on the surface of solid particles results in the formation of ordered polymer layers, which play the role of crystallisation centres in crystallising polymers, and of regions determining the structure formation in the entire system in amorphous polymers; the capacity of oligomers and monomers for polymerisation is also important.[92,93] According to modern ideas concerning filled polymer systems, the presence of such layers increases the heterogeneity of the system and improves its mechanical properties as a result of the decrease in the energy of cohesion in boundary layers and the possibility of the relaxation of stresses.[94]

Metallopolymer coatings consist of a polymer base in which metallic particles are distributed. Typical structures of composite metallopolymer deposits are illustrated in Fig. 7. Fig. 7*a* represents a coating obtained by the electrophoretic-electrochemical deposition of dispersions of epoxide and polysulphide oligomers and lead on a steel plate (D_c = 9 A m^{-2}, deposition time 120 s). The ratio of the polymer components is 8.5 : 1.5 and the concentration of the metal is 60 wt.%. The bulk of the oligomers exist in the form of globules 500–1000 A in size. The interaction of the polymers with the colloidal metallic particles on the surface of the latter results in the formation of compacted polymer layers (Fig. 7*b*). They are clearly observed after etching the coating in active oxygen (Fig. 7c). The chemisorption interaction and the formation of surface compounds at the metal–polymer boundary have been confirmed by IR spectroscopic studies.[15,16]

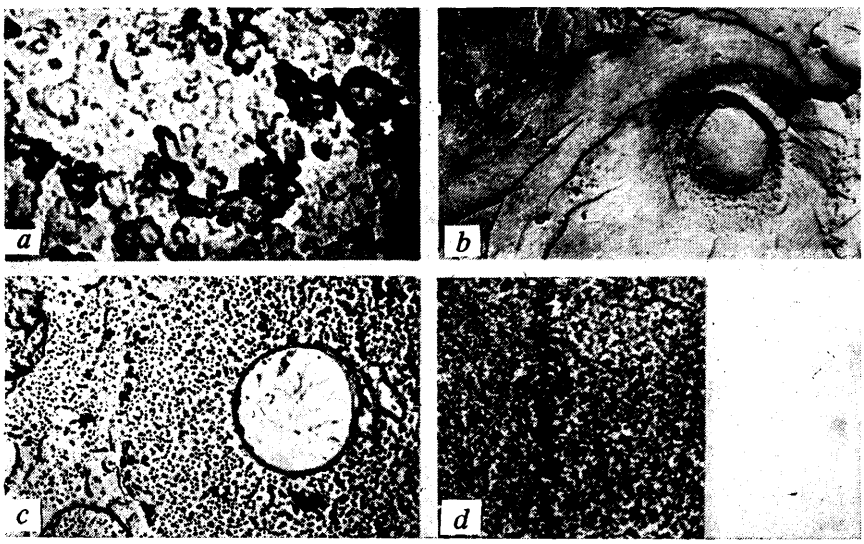


Figure 7. Electron micrographs:[12] *a*) a metallopolymer coating (magnification ×8400); *b*) region near a metallopolymer particle (magnification ×70000); *c*) ditto after etching; *d*) metallopolymer coating on which a profile line has been drawn.

It has been established by X-ray diffraction studies that the partial deformation of the crystal lattice of the metal (for example, reflections characteristic of the β-form of zinc appear) and the change in the packing density of the coatings are a consequence of the chemisorption interaction at high metal concentrations in the metallopolymer coatings.[67]

The formation of interfacial boundary layers of polymers on the surfaces of metallic particles is an important factor, which tends to impart anticorrosion properties to the coatings. Their corrosion stability is associated not only with the inhibiting and protective properties of the metals but also with the hindrance of the access to electrolytes as a consequence of the shielding of the surfaces of the coatings by the surface compounds formed. The degree of perturbation of the corrosion process is then determined by the composition of the coating.

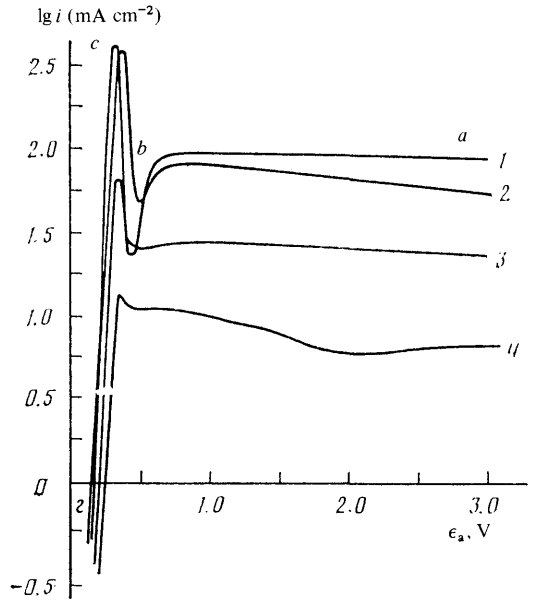


Figure 8. Polarisation curves for the anodic dissolution of copper electrodes in a solution of 200 g litre^{-1} $CuSO_4$ and 90 g litre^{-1} of H_2SO_4: *1)* unprotected electrode; *2)–4)* electrodes with a metallopolymer coating based on an organosilicon oligomer with copper contents of 80, 64, and 44% respectively.[64]

The protective properties of the metallopolymer coatings can be illustrated by comparing the electrochemical behaviour of copper electrodes without a coating and with a metallopolymer coating based on an organosilicon oligomer and copper. Fig. 8 presents the results of a potentiometric study of such electrodes.[64] The metallopolymer coatings were produced by the simultaneous deposition of copper and an emulsion of an organosilicon oligomer (D_C = 7.5 A m^{-2}, τ = 180 s). For small deviations of the equilibrium potential of the electrodes into the anodic region, a sharp rise in the current is observed. After the attainment of certain critical current and potential, the electrodes are passivated. The polarisation curves *1* and *2* are characterised by a maximum and a minimum (points *b* and *c*). The "*ab*" region corresponds to the active dissolution of the metal and the "*cd*" region corresponds to its passive state; the copper dissolution process almost ceases under these conditions. The maximum on the curves is reduced with increasing content of the polymer in the metallopolymer layer and almost disappears for a copper content of 44%, while the passivation potential is reached at lower current densities: at 315.2 mA cm^{-2} for the copper electrode and at 12.6 mA cm^{-2} for the metallopolymer electrode with a copper content of 15%. The rate of corrosion of the copper electrode is 5–6 times greater than that of the metallopolymer coating containing 44% of copper.

The retardation of the dissolution of electrodes with coatings based on oligomers having the COO^-, NH_3^+, $H_2C—CH—$ (O), etc., functional groups is very marked. At lead and copper concentrations in the range 55–68% and zinc and cadmium concentrations in the range 68–73%, the dissolution of the metal ceases almost completely.[12,64] With increase in the metal content in the coating, the shielding of the surface diminishes and, furthermore, the adhesion of the coating to the support is weakened. The conditions for the preparation of metallopolymer coatings based on the above metals and also epoxide and polyether resins as well as organosilicon and polyether varnishes have been described.[12,18,64,70,96]

The metallopolymer coatings with the optimum composition obtained to date have corrosion stabilities superior to those of polymer coatings and the corresponding galvanic coatings (Table 5).

Table 5. The corrosion and mechanical stabilities of polymer, metallic, and metallopolymer coatings.[18]

Composition of coating	Σ, mm	A_1, days	A_2, days
Polymer coating based on E-41 and E-30 epoxide resins	1–2	70	60
Galvanic coating based on lead	—	90	78
Metallopolymer coating based on a mixture of epoxide resins with 60% of lead	1	110	96

Notation: Σ is the bending strength, A_1 the stability in 3% NaCl solution, and A_2 the stability in a chamber with 100% humidity.

The corrosion stability of metallopolymer coatings is greater the stronger the bond between the functional groups of the oligomer and the metal, for example, zinc.[74] It has been noted[95] that, when phenol-formaldehyde oligomers are used, the region of the maximum stability in corrosive media shifts towards higher metal concentrations as the bond between the polymer and the metal weakens in the sequence inner complex (chelate) > ionic > coordinate (via amino-groups) > donor–acceptor (via the OH group) > no chemical bond (ester group). The decrease in the number of epoxide rings on formation of metallopolymer coatings based on epoxide oligomers and the Zn–Pb alloy is accompanied by a sharp fall of corrosion stability.[18,98]

The dependence of the corrosion stability of coatings based on phenol-formaldehyde oligomers and zinc on their content of carboxy-groups passes through an extremum.[74,97,99] This is associated with the fact that, in the region of maximum corrosion stability of the coatings, the concentration of

the functional groups corresponds to the most favourable combination of two mechanisms of protection: the protective mechanism and the insulating mechanism involving the formation of surface compounds.

The introduction of colloidal metals into polymer coatings makes it possible to improve considerably the physicomechanical properties (to increase the adhesion and impact strength) and antifriction properties (to decrease the coefficient of friction and the wear of the material).[15] The thermal and electrical conductivities of metallopolymer coatings can be regulated within wide limits by varying the concentrations of the metals.

The electrical conductivity and the enhanced corrosion stability of metallopolymer materials permit their use as anticorrosion layers (primer) on which polymer compositions or industrial paints, for example, VAS-1162 and EP-2100, are subsequently electrodeposited. Data typical for two-layer metallopolymer–polymer coatings are presented in Table 6 for two industrially manufactured materials (VAS-1162 and EP-2100) with metallopolymer anticorrosion layers (primers) based on lead and the lead–copper alloy. The stability of such a system comprising two-layer coatings during their tests in chambers with 100% humidity and a 5% salt mist is higher by a factor of 2–3 than that of the single-layer industrial coatings of the same thickness (Table 6).

Table 6. The corrosion stabilities of polymer and metallopolymer coatings in a chamber with a 5% salt mist (NaCl)*.[98]

Composition of coating		τ, h
layer II	layer I	
Industrial materials: VAS-1162	—	176
EP-2100	—	176
Lead-based (60 wt.%) metallopolymer primer	VAS-1162	520
	EP-2100	520
Metallopolymer primer based on a lead–copper alloy (60%)	VAS-1162	>615
	EP2100	>615

*The thickness of the coatings was 45 μm.

Table 7. Dependence of the dielectric strength of polymer and two-layer metallopolymer-polymer coatings on the deposition time.[59]

Type of coating	Dielectrical strength (kV) for different deposition times (min)					
	0.5	1.0	1.5	2.0	2.5	3.0
Polymer coating based on a mixture of the E-30 and E-41 epoxide resins	0.8	1.5	1.75	2.0	1.8	1.4
Two-layer coating (first layer—metallopolymer based on a mixture of resins and lead; second layer—mixture of epoxide resins).	2.0	2.7	3.2	3.5	3.7	3.8

An important application of two-layer metallopolymer-polymer coatings involves the creation of highly effective electrically insulating coatings. The results of tests of the electrical strength of polymer and metallopolymer-polymer coatings are presented in Table 7. For the same thickness (40 μm), the dielectric strength of composite two-layer coatings is increased by a factor of two.[12,59] The presence of the metallopolymer layer ensures an increase in adhesion to the support and hence an improvement in the anticorrosion properties and also in the homogeneity, uniformity, and the specified thickness of the coatings along the edges of the given articles.

The electrically insulating properties of the two-layer coatings do not change after periodic alternation of the polarity of the electric field.

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Thus the simultaneous use of two classical phenomena—electrophoresis and electrolysis—had led to the development of new methods of formation of metallopolymer structures and materials. The possibility of regulating the kinetics of electrode processes with the aid of the electrophoretic deposition of polymers–electrophoretic polarisation—is of considerable interest from the standpoint of the electrochemical preparation of metallic powders and the anodic passivation of metals.

Further development of this field requires the solution of a number of problems in colloid chemistry, electrochemistry, and the physical chemistry of filled polymers, which include the problems of the stability of dispersed systems in electric fields, of the electrocrystallisation of metals in polymers, and of the interaction of polymers with colloidal metals.

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