Translated from *Uspekhi Khimii*, 48, 2240-2261 (1979) U.D.C. 541.13:547.921.6

The Formation of Coatings in the Anodic Electrodeposition of Water-Miscible Lacquer Systems

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The physicochemical principles of the formation of polymeric coatings in the electrodeposition of water-miscible compositions based on carboxyl-containing oligomeric electrolytes are described. The mechanism of the formation of the deposit on the anode and the film formation processes on various metallic supports are considered.
The influence of the composition of the system and the deposition conditions on the electrodeposition mechanism and the properties of the coatings are discussed. It is shown that electrodeposition is one of the ways of creating an ordered structure in the formation of polymeric coatings, which ensures a higher rate of relaxation processes.
The bibliography includes 104 references.

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I. INTRODUCTION

Lacquer coatings are thin polymeric films bound to the support by adhesion forces. The mechanism of their formation includes the formation of local bonds between the active groups of the polymer molecules and the surface of the support. This results in a retardation of the relaxation processes and the occurrence of internal stresses which lower the lifetime of the coatings. The rate of relaxation processes and the cause of the stresses depend on the conformations of the molecules in solution, on the nature of the supermolecular structures arising in the coating at a particular stage in the formation of macromolecules, and also on the number and nature of the bonds between them.

This review deals with the formation of coatings from water-miscible lacquer materials based on water-soluble oligomeric electrolytes when they are electrodeposited on a support[1,2]. This is a new method of colouring, which appeared at the beginning of the 1960's as a special procedure for the deposition on a metal of aqueous lacquer systems[3-9], whose application has been extremely limited hitherto owing to the difficulty of their conversion into a coating in view of the specific features of water as a solvent. A characteristic of this method of colouring, in contrast to traditional methods based on the evaporation of solvents, is that the coatings are formed in two stages. Initially a water-insoluble deposit is formed on the anode in the field of a direct current, the anode consisting of the article to be coloured, and subsequently, in the course of thermal hardening, a three-dimensional network is formed from the virtually dehydrated oligomeric system. The review deals with the mechanisms of the processes occurring in this system.

II. CHARACTERISTIC FEATURES OF THE FORMATION OF COATINGS IN THE ELECTRODE POSITION OF WATER-SOLUBLE FILM-FORMING AGENTS

1. The Formation of a Deposit on the Anode

The film-forming agents used as binders in lacquers for electrodeposition consist of water-soluble carboxyl-containing oligomeric electrolytes. Their acid form is weakly dissociated; after the neutralisation of the carboxy-groups by organic amines (ammonia), they become water-soluble and capable of dissociation via the mechanism[7]

$$RCOONH_4 \rightleftarrows COO^- + NH_4^+ \quad ,$$

where $RCOO^-$ is the film-forming component converted into the anionic form. The diphilic structure of the molecules of the film-forming agents makes it possible to compare them with a set of low-molecular-weight surfactants whose hydrophobic component consist of a polymer (oligomer) chain and the hydrophilic component consists of COOH groups.

It has been established, on the basis of the surface tensions, electrical conductivities, and light scattering in aqueous solutions of a number of film-forming agents as a function of concentration[10], that aqueous solutions of neutralised film-forming agents at the concentrations used for electrodeposition (6–10%) are either micellar solutions containing ionised micelles (together with individual ions) or polyelectrolytes, in which neutral molecules (or their associated species) and ions are involved in an equilibrium controlled by the dissociation constant. In the first stage

of the development of the method of colouring by electrodeposition the mechanism of the formation of the deposits on the anode from such systems was obscure.

Numerous studies were carried out during this period and general hypotheses were put forward concerning the process mechanism, by analogy with galvanic processes as well as the electrophoretic process for the formation of coatings[11-19]. It was to be expected that the segregation on the anode of a polymer phase from the solution of a carboxyl-containing polyelectrolyte is associated with electrochemical processes in the region near the electrode under the influence of the electric current.

Anodic processes in an aqueous medium have been thoroughly investigated in relation to a number of metals[20-22]; in the case of metals incapable of being passivated these involve anodic dissolution:

$$M \rightarrow M^{n+} + ne \quad , \qquad (1)$$

while in the case of metals which can be passivated as well as certain inert electrodes such as platinum and graphite the relevant process involves the electrolytic dissociation of water:

$$H_2O \rightarrow 2H^+ + 1/2O_2 + 2e \qquad (2)$$

At high pH values reaction (2), which can occur in solutions at pH $\leq$ 11.5, is replaced by the discharge of hydroxide ions:

$$2OH^- \rightarrow 1/2O_2 + H_2O + 2e \quad . \qquad (3)$$

Apart from reactions (1)–(3), other electrochemical processes can occur on the anode in the electrodeposition of water-soluble film-forming agents—anodic oxidation of the metal (for example in the colouring of aluminium) as well as the decarboxylation and oxidation reactions of the organic molecules:

$$2RCOO^- \rightarrow R{-}R - + 2CO_2 + 2e \quad , \qquad (4)$$

$$RCOO^- + H_2O \rightarrow ROH^- + CO_2 + 2e \quad , \qquad (5)$$

$$\overset{|}{-}CH_2 + \cdot H_2O \rightarrow HCOH + 2H^+ + 2e \quad . \qquad (6)$$

It is believed[23] that the formation of a deposit on the anode under the electrodeposition conditions takes place as a result of the electrochemical discharge of the anions of the film-forming agent associated with decarboxylation as in the Kolbe synthesis in accordance with reaction (4).

Beck[24,25] calculated the change in the concentration of hydrogen ions in the anodic compartment during the electrodeposition of water-soluble oligomers. In the electrodeposition from solution at pH 8 and a current density of 2.5 mA cm^{-2} the pH in the anodic compartment falls to 2, which corresponds to (or is lower than) the pH at which deposits are formed in the electrodeposition of anionic water-soluble film-forming agents.

In order to elucidate the mechanism of the formation of the deposit on the anode in the electrodeposition of water-soluble film-forming agents (in relation to VBFS-4 resin, VML oil, rezidrol and water-soluble acrylic carboxyl-containing film-forming agents), the chemical composition of the films electrodeposited on anodes made of different metals was analysed by infrared spectroscopy (before thermal hardening).[29-30,44] It was established that, in the electrodeposition of the film-forming agents on anodes made of metals such as copper, cadmium, and zinc, the products are predominantly the salts of the binders, while in the electrodeposition on insoluble anodes and on steel mainly their acid form is produced. The acid form of the film-forming agents is produced as a result of their interaction with the H^+ ions generated in the anodic compartment by reaction (2), while the formation of the salt form is associated with reaction (1). It was observed that a steel anode dissolves at the rate of 0.25 and 0.18 g m^{-2} min^{-1} in the electrodeposition of the FL-149E enamel and the FL-093 primers respectively. Chemical analysis established the presence of iron in the electrodeposited film. X-Ray diffraction analysis showed that the thermally hardened coating contains iron in the form of the oxides Fe_2O_3 and Fe_3O_4 and not as products of the interaction with the film-forming agents. The oxides were probably formed during drying from the iron hydroxides deposited on the anode.

It has been suggested[27] that the difference between the mechanisms of electrodeposition on anodes of different types can be accounted for by the different solubilities of the salt and acid forms of the film-forming agents, on the one hand, and the hydroxides of the metal of the support, on the other. According to the solubility products (SP) of the hydroxides, iron(III) hydroxide is deposited most readily ($SP_{Fe(OH)_3} = 3.8 \times 10^{-38}$), while zinc hydroxide is deposited with the greatest difficulty ($SP_{Zn(OH)_2} = 5 \times 10^{-7}$). The concentration of the metal ions at the copper, cadmium, zinc, and other metal anodes is sufficient for the deposition of the binders in the salt form. It is noteworthy that the electrodeposition of the VML oil and rezidrol is accompanied by the partial oxidation of the double bonds, as shown by the decrease (up to complete disappearance) of the bands at 3020 and 997 cm^{-1} in the spectra of the resulting electrodeposited films.

In the electrodeposition of acrylic film-forming agents[28-30] the deposit is produced on the steel anode as a result of the interaction of the film-forming agent with both hydrogen and metal ions produced in the anodic dissolution of the electrode. If the electrodeposition is carried out on a steel anode over a long period (>3 min), then in the case of rezidrol the deposit is found to contain a certain amount of the salt form owing to the secondary interaction between the acid form of the film forming-agent produced and the metal hydroxides present in the film.

Thus the mechanism of the formation of a deposit on the anode (as the acid or salt form of the film-forming agent) depends on the nature of the metal on the surface being coloured, the chemical composition of the film-forming agent, and the conditions of the electrodeposition process (i.e. is determined by the solubility of the acid or salt form of the film-forming agent under the given electrodeposition conditions). The mechanism of the electrodeposition consists in the loss of solubility by the film-forming agent in the anodic compartment on interaction with the hydrogen or metal ions formed as a result of the primary electrochemical reactions in the electrolysis of water and the anodic dissolution of the metal. Reactions (4) can take place only on insoluble anodes at a rigorously defined temperature and pressure[31]. Oxidation of the film-forming agent plays an insignificant role. Furthermore, the discharge of ions on the surface of the anode should have ceased immediately after the segregation of a monomolecular organic layer, lacking in electronic conductivity, which was not confirmed by observations on the growth of the thickness of the coating.

Analysis of the composition of the gas involved on the anode[32-34] and the determination of the range of electrode potentials[35-38] at which electrodeposition takes place established that the current is mainly consumed in reactions (1)–(3). The partial oxidation at the anode of the

amines used as neutralisers of the film forming agents can also be included among secondary reactions[32,38]. This mechanism of the formation of a deposit on the anode agrees satisfactorily with the fundamental electrochemical studies of the electrodeposition of carboxyl-containing polyelectrolytes carried out in recent years[35-38]. These data established that, in the electrodeposition of polyelectrolytes on steel and also on phosphated steel, the main electrode reaction in the absence of activators of anodic dissolution is evolution of oxygen as a result of the oxidation of water molecules; at the same time the binder may be oxidised, which also leads to the formation of H^+ ions in the region near the anode.

Since the solution is stirred in the course of the electrochemical decomposition, the bath with the working solution may be regarded as a volume with a constant concentration[36]. A difference between concentrations is observed only at the interface where a diffuse double layer (Nernst layer) is "stuck" to the electrode. In this quasi-stationary layer species are transported via diffusion, which arises owing to the concentration gradient due to the discharge of the ions on the electrode and the migration of protons to the cathode as well as the migration of ions under the influence of electrical forces. Calculations have shown[36] that the thickness of the anodic layer of hydrogen ions is 10^{-2} cm. The film-forming agent loses its solubility in water on interaction with the precipitant ions in the layer near the anode. The deposits formed on the anode are highly concentrated two-phase systems. These are colloidal structures consisting of globular particles, whose size varies from 0.1 μm to several hundred μm, depending on the type of the film-forming agent and the process conditions[39,40].

The electrodeposition process takes place in a relatively dilute medium (6–15%), but the electrodeposits consist of highly concentrated systems. The dry residue of the electrodeposited films amounts to 94–98% and the electrodeposition conditions have only an insignificant influence on this proportion[36,39,40]. The hypothesis of the decisive role of electroosmosis in the mechanism of the dehydration of anodic deposits, which remained current for a long time, was not confirmed when the degree of electroosmotic dehydration was calculated from electrochemical equations[36] although electroosmosis undoubtedly takes place. Since the system passes through a metastable state on formation of a deposit, water is evidently removed also as a result of syneresis. The deposit is dehydrated also in consequence of the decomposition of water in the diffuse layer near the anode[36]; the protons evolved are transported through the film via diffusion and migration. According to Beck's view[36], the negative ions of the film-forming agent still fixed in the deposit can be regarded as bound to mobile protons, as happens in weakly acidic ion-exchange resins; the protons are expelled to the surface of the film, which ensures an increase of its thickness.

When the process is carried out under the conditions of a constant current density (galvanostatic conditions), the rate of electrodeposition can be expressed by adding the weight of the deposit on the anode per unit time. The overall form of the experimental time variation of the increment in the weight of the deposit is illustrated in Fig. 1*a* for a number of film-forming agents[36,38,39]. The relation along section *1* (Fig. 1*a*) is linear, but the corresponding straight line does not pass through the origin of coordinates. The induction period at the beginning of the process, where the coating is not formed, is necessary to create in the anodic compartment a concentration of H^+ of M^+ ions sufficient to precipitate the film-forming agent. The induction period and the slope $\tan\alpha$ depend on the nature of the film-forming agent and on the process conditions. For the same film-forming agent in a bath without stirring, there is a qualitative relation between the duration of the induction period and the reciprocal of the square of the current density. Theoretically one gram-equivalent of the precipitant ions evolved in the electrochemical reaction should neutralise one gram-equivalent of the macroanions. Thus

$$q = 5.6 \times 10^6/\text{A.N.} \times aF, \qquad (7)$$

where A.N. is the acid number of the film-forming agent (mg KOH/g resin), a the degree of neutralisation, and F the Faraday. Hence it follows that the quantity q, called the "conventional current yield", should be a constant characterising the given carboxyl-containing polyelectrolyte. However, experimental tests showed[38-39] that q and $\tan\alpha$ (for the given current density) depend on the concentration of the film-forming agent, the stirring conditions in the bath, the pH, temperature, the conversion of the film-forming agent into an insoluble state on partial neutralisation of the ionised carboxy-groups, the polydispersity with respect to the molecular weight and composition, etc. It has been established for acrylic film-forming agents[41,42] that, with increase in the number of carboxy-groups in the copolymer per unit molecular weight, in the degree of neutralisation of the binder, in the pH of the system, in the rate of stirring, and, when the temperature is reduced, also with increased current density[40], the induction period increases and $\tan\alpha$ falls.

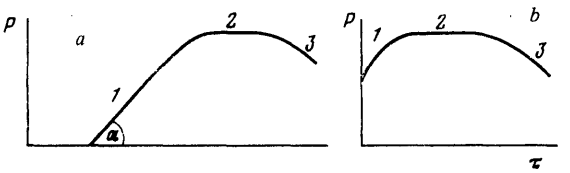


Figure 1. Schematic illustration of the dependence of the increment in the weight of the deposit on the anode P as a function of the process time τ [7,29,41] under different conditions: *a*) i = const.; *b*) u = const.

When the process is carried out under constant-potential conditions (potentiostatic conditions; Fig. 1*b*), there is a high initial current density, so that the induction period does not play an important role along section *1*. The thickness of the coating increases with time. Along section *2*, the thickness of the film does not increase for a long time (up to 5–10 min, depending on the type of film-forming agent and current density) and then begins to decrease (section *3*). The retardation of film growth is attributed[36] to the hindrance of ion transport through the film, which is regarded as the rate-limiting process. The presence of maxima and minima on the $i(\tau)$ and $u(\tau)$ curves has been observed by a number of workers[35,36,49] and some of them believe that this is caused by dielectric breakdown[44]; other studies established a relation between the heat evolution in the film and the existence of the extrema[43,45]. It has been observed[40,46] that the presence of section *3* on the curves in Figs. 1*a* and 1*b* is associated

with the stripping of the deposit from the anode owing to the increase of the amount of heat evolved during the electrodeposition. This was established in a study of the structural-mechanical properties of the films formed on the anode under different electrodeposition conditions.

2. The Influence of Structural-Mechanical Properties of the Film-Forming Agents on Their Electrodeposition

The formation of polymeric coatings proceeds via a structure formation stage[1-5]. The structure formation in the solution from which the coating is produced influences the rate of inhibition of relaxation processes. During electrodeposition, a structure is produced on formation of the deposit on the anode before the onset of thermal hardening. The ability of the system to give rise to relaxation processes, on which the formation of monolithic defect-free films depends, can be inferred from structural-mechanical properties.

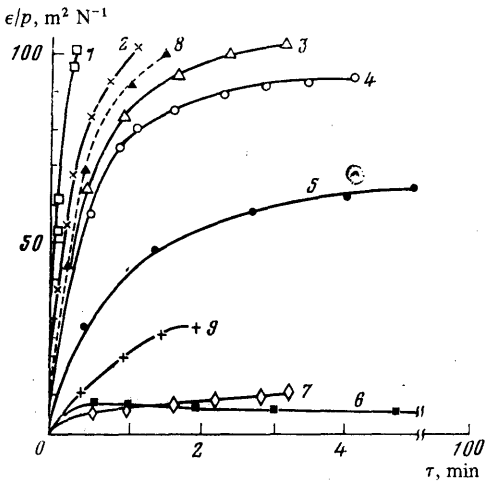


Figure 2. The development of the shear deformation (ϵ/p) of the electrodeposits with time (t) ($p = 2$ N m^{-2}):[46] 1) VML oil; 2) VA-105 rezidrol; 3) VA-133 rezidrol; 4) polyacrylate + 3% butanol; 5) polyacrylate + 2% butanol; 6) polyacrylate without butanol ($p = 20 \times 10^3$ N m^{-2}); 7) VBFS-4 resin + 3% of 2:1 mixture of butyl and isopropyl alcohols; 8) VBFS-4 resin + VML oil + 3% of 2:1 mixture of butyl and isopropyl alcohols; 9) VBFS-4 resin + VML oil with a reduced content of solvents.

In the formation of coatings by the electrodeposition method the structural-mechanical properties of the deposits on the anode play a special role associated with their influence on the mechanism of the electrical insulation of the anode. The rheological characteristics of the electrodeposits obtained from systems of water-soluble film-forming agents, differing in their chemical nature and in the presence of added organic solvents, have been investigated[45-47]. The form of the deformation curves (Fig. 2) leads to the conclusion that the electrodeposits exhibit different rheological properties. Thus deformation curves for rezidrol and acrylic film forming-agents containing added organic solvents have sections with conventional instantaneous elastic and plastic deformation, while the VML oil flows and the VBFS-4 resin is not deformed at all owing to its brittleness. The capacity for deformation of acrylic film-forming agents without added organic solvents is weak. There is a corresponding difference in the behaviour of the above systems in electrodeposition. Monolithic defect-free films are formed from rezidrol and the VML oil. The electrodeposition of the VBFS-4 resin and acrylic film-forming agents from systems without organic solvents leads to the formation of thin porous coatings. When organic solvents are added to these systems, the nature of the porosity changes. With increase in the amount of solvent in the system, the pores ("craters") in the coating become smaller and then disappear altogether. Under these conditions, the electrical resistance of the anode diminishes and there is a corresponding increase in the thickness of the coating. The introduction of organic additives into the system based on the VML oil (the deposit exhibits an appreciable irreversible deformation) leads to the formation of bulges on the coating and to a decrease of the electrical potential during deposition.

The increased hindrance to the coalescence of the electrodeposited species with increasing rigidity of the film-forming agent leads to the retardation of the removal of oxygen bubbles from the surface of the anode, to an increase in the resistivity of the latter, and to the consequent formation of thin porous coatings (the pores are sites where oxygen bubbles are located)[47-51]. Conversely factors promoting the coalescence of particles (for example, the introduction of organic solvents plasticising the electrodeposits) causes an increase of the capacity of the system for undergoing relaxation processes, which leads to the "healing" of the pores, to a decrease of the resistivity of the anode, and to an increase of the thickness of the coatings. However, a high plasticity of the system is also undesirable from the standpoint of the electrodeposition process. This has been shown[46] by comparing the VML oil, the VA-105 rezidrol, and the VA-133 rezidrol, which differ in the rheological characteristics of their electrodeposits and the deposition parameters (Fig. 3).

Direct measurement of the temperature of the anode during the electrodeposition process with the aid of a Chromel–Copel thermocouple welded into the anode established[43] that during electrodeposition the temperature of the anode rises up to 70–80°C depending on the electrical parameters. Such heating in the case of the highly plastic VML oil (Fig. 3) leads to the formation of bulges on the surface of the coating and, on further increase of the potential, the coating flows off the surface of the anode. The optimum potential in the electrodeposition of the VML oil is 30–40 V. The high viscosity of the rezidrol deposit (Figs. 3*b* and 3*c*) makes it possible to increase the potential considerably during electrodeposition (up to 300 V) for the VA-133 rezidrol.

Thus a significant factor in the formation of coatings by electrodeposition is the viscosity of the deposit formed for low shear stresses. From this it also follows that one of the causes of the differences between films electrodeposited from high-resistance lacquer materials at high potentials (hundreds of volts) and low-resistance materials (deposition potential of tens of volts) consists in the difference between the structural-mechanical properties of their deposits, which play an important role in the mechanism

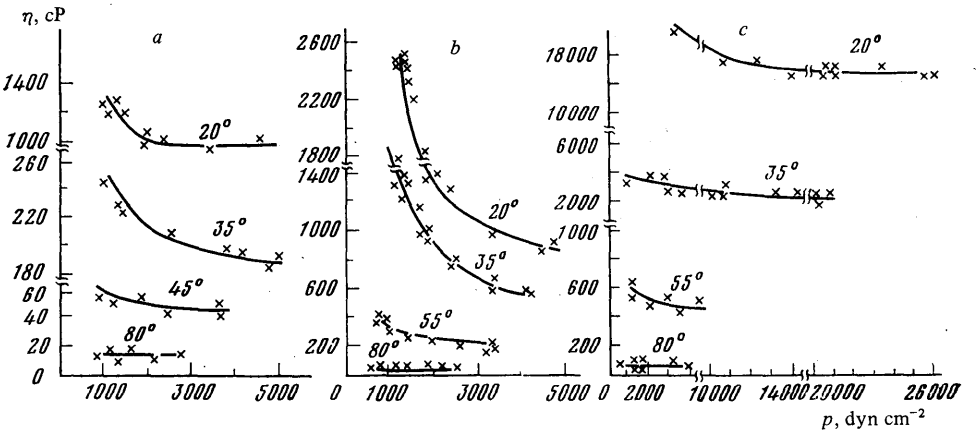


Figure 3. Dependence of the viscosity η of electrodeposits based on different materials as a function of the stress p corresponding to the slipping of the deposits[46]: *a*) VML oil; *b*) VA-105 rezidrol; *c*) VA-133 rezidrol.

of the electrical insulation of the anode during electrodeposition[45].

3. The Mechanism of Film Formation in the Electrodeposition of Water-Soluble Film-Forming Agents

(a) The influence of the method of deposition of water-soluble film-forming agents on the support. It has been established by infrared spectroscopy that the mechanism of film formation in the production of coatings by methods based on the evaporation of solvents (pouring, spraying) and on electrodeposition is in principle the same at the molecular level and is associated mainly with oxidative polymerisation (VML oil[27], rezidrol[52]), with formation of ester linkages via carboxy- and hydroxy-groups (VML oil, VBFS-4 resin, and partly rezidrol), and also (in the case of acrylic film-forming agents) the interaction of hydroxymethyl groups with carboxy- and amide groups[53]. However, in electrodeposition the formation of a three-dimensional network takes place to a greater extent than in the formation of coatings by pouring and the difference is greater the lower the hardening temperature (Table 1).

Electron microscope study of coatings has shown that electrodeposited coatings are structurally more homogeneous and that the size of the structural elements and the distance between them is smaller than in the formation of coatings by pouring or spraying (Fig. 4). With increase of the hardening temperature, the size of the structural elements of the coating and the distance between them diminish, but in electrodeposition there is a greater number of structural elements per unit surface than in the pouring method over the entire experimental temperature range (from 20° to 250°C). Owing to the smaller dimensions of the structural aggregates, better conditions are probably established in electrodeposition for a more complete interaction between the structural elements on the surface via the reactive groups than in the pouring method. Apart from the smaller size of the structural elements of the coating, the acceleration of the film formation process in electrodeposition is associated with the regeneration of the reactive carboxy-groups on formation of a deposit on the anode (in the pouring method this occurs only during thermal hardening) and also, in the case of oily binders, with the preliminary oxidation of the film-forming agent on the anode.

Table 1. Dependence of the molecular weight of the section of the chain between the effective nodes of the three-dimensional network (M_C) in the formation of rezidrol coatings on the hardening temperature[52].

Method of colouring	Hardening temperature			
	130°	180°	200°	220°
Pouring method	3792	975	371	308
Electrodeposition method	371	280	241	238

The presence of a homogeneous fine globular structure of the electrodeposited coating creates conditions better than in other deposition methods for the acceleration of relaxation processes. This is confirmed by data obtained in the study of the thermal conductivities of coatings. It has been established[27] that the thermal conductivities of electrodeposited coatings are greater than those of the coatings formed by spraying or pouring. As a result, the electrodeposited coatings have smaller internal stresses and hence better physicomechanical properties. Indeed, the resistance to wear and adhesion are superior in electrodeposited coatings to those of coatings obtained by the pouring and spraying methods[52]. The available literature data[54], suggesting that the properties of coatings obtained by electrodeposition and spraying do not differ, are based on a comparison of properties of coatings which, although obtained from water-soluble systems, were produced in different media (a comparison was made of coatings obtained by electrodeposition from an aqueous medium and deposited by spraying from an acid paste diluted with organic solvents). Tests on the protective properties of the coating showed that electrodeposited

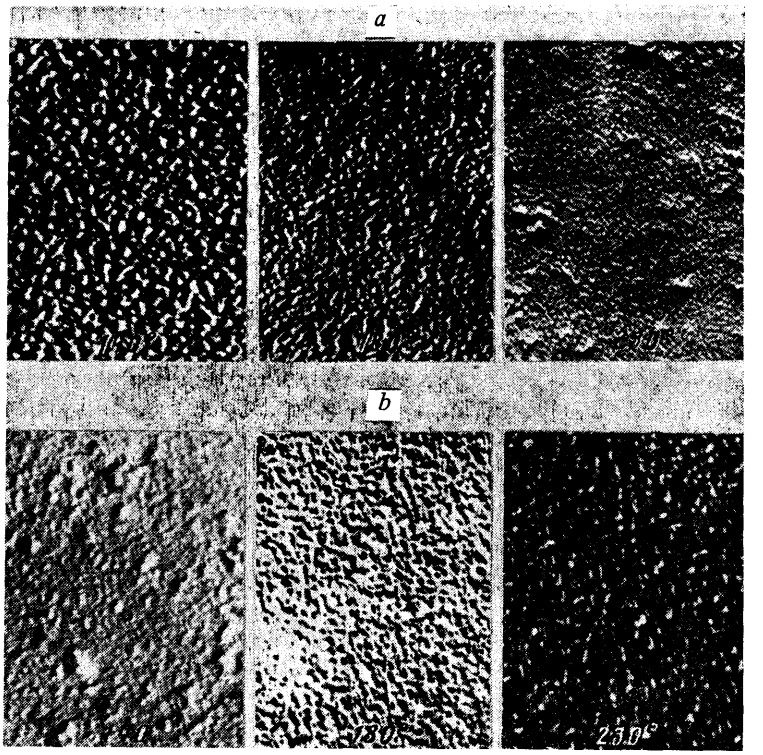


Figure 4. Electromicroscope structure of coatings based on rezidrol[52]: *a*) formation by electrodeposition; *b*) formation by the pouring method. Magnification 1 × 32 000

coatings exhibit a more satisfactory resistance to water and salts than films produced by other deposition methods[52].

All these factors suggested a longer lifetime of the electrodeposited coatings compared with those produced from the same lacquer systems by other deposition procedures.

It has been established in a number of studies[55,56] that the lifetime of polymer coatings obeys the relation

$$t = A e^{-\beta x},$$

where t is the time before the breakdown of the coating, x a characteristic of the state of the coatings which may be a number which represents the estimated state of the coating, the disruptive or internal stresses, the change in the content of functional groups, etc., A = the logarithm of the time required for the attainment by the coating of the state estimated in terms of a specified number, and β is the rate of change of the state of the coating. Thus, in terms of logarithmic coordinates, there is a linear relation between $\lg t$ and x.

It follows from the data in Fig. 5 that the protective properties of the electrodeposited coating persist appreciably longer than those of the coating produced by spraying when tests are made for water resistance (Fig. 5*a*); in tests carried out in a salt mist chamber (Fig. 5*b*) the change in the properties of the coatings obtained by both electrodeposition and spraying begins simultaneously but the electrodeposited coatings lose their protective properties one and a half times more slowly than those produced by spraying[57].

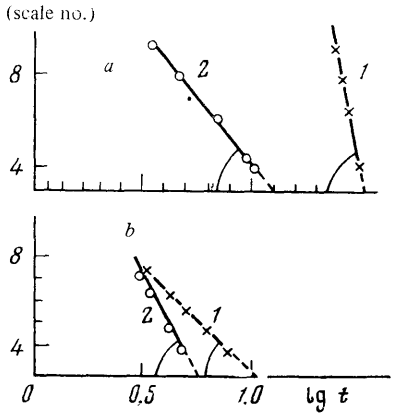


Figure 5. Variation in the state of the coatings based on the FL-093 primer deposited by electrodeposition (line *1*) and spraying (line *2*) in the course of ageing in a hydrostat (*a*) and in a salt mist chamber (*b*).[57]

(b) The influence of the nature of the metallic support. A characteristic feature of the coatings, which distinguishes them from other polymeric materials, is that they are formed on a support. The influence of the nature of the support on the structure and

properties of coatings produced by the methods based on solvent evaporation is determined both by the overall area of contact and by the shape of the surface, the number and nature of bonds at the boundary, and the nature of their distribution.

In oligomeric systems the formation of a structure inhomogeneous with respect to thickness and area takes place in consequence of the adsorption interaction of the oligomers with the support before the start of polymerisation. Furthermore, as shown above, in electrodeposition the nature of the support influences the chemical composition of the deposit formed on the anode.

It has been shown[58] that electrodeposition on steel and aluminium proceeds via a mechanism involving the formation of the acid form of the film-forming agent. The electrodeposition on aluminium is characterised by a lower degree of oxidation of the film-forming agent on the anode, as a result of which the oxygen evolved in the electrolysis of water is consumed to a greater extent on aluminium anodisation processes. Electrodeposition on copper involved the formation of the salt form of the film-forming agent. The above specific features of the formation of the electrodeposit on anodes of different kinds are responsible for the differences between their structural-mechanical properties (Table 2).

Table 2. The influence of the nature of the support on the conventional viscosity η of rezidrol electrodeposits and on the M_C for coatings formed on different metals[58].

Metal	$10^{-5}\eta$, Pa s	M_C at the hardening temperature			
		130°	180°	200°	225°
Copper	2.000	157	76	49	25
Steel	0.480	184	98	87	69
Aluminium	0.324	374	280	241	225

The conventional viscosity of the deposit, calculated from the rate of development of the shear deformation between two plane-parallel plates, is a maximum for a copper support. The greater conventional viscosity of films on steel compared with aluminium can be accounted for by the greater degree of oxidation of the film-forming agent. During thermal hardening on steel and aluminium, the formation of a three-dimensional network in oils is associated with oxidative polymerisation.

In a coating on copper double bonds are retained even at 275°C. The cause of this is the blocking of the double bond by copper ions, which can form a coordinate bond with the latter. Nevertheless data obtained by the direct determination of the molecular weight of the section of the chain between the effective nodes of the three-dimensional network (M_C) showed that the greatest density of cross-links obtains in the coating electrodeposited on copper. These phenomena are associated with the fact that the mechanism of film formation in electrodeposition on copper is in principle different from that of film formation on steel and aluminium and consists in the formation of ionic and coordinate bonds with copper ions.

The results of the determination of the mechanical properties of the coatings during hardening agree satisfactorily with the film formation mechanism examined above[58]. Coatings obtained on steel and aluminium supports exhibit the greatest and smallest resistance to wear. The formation of a three-dimensional network on a copper support via ionic bonds is responsible for the higher resistance to wear of the coatings at a low hardening temperature and the smaller influence of the hardening temperature on the mechanical properties as compared with steel. The lower resistance to wear of the coatings on copper, compared with steel, at temperatures above 150°C is associated with their greater rigidity and their coarsely globular structure, which retard the relaxation processes.

III. THE MECHANISM OF THE ELECTRODEPOSITION OF THE PIGMENT COMPONENT OF WATER-MISCIBLE LACQUER MATERIALS

Apart from film-forming materials, the most important components of the lacquer system are pigments and fillers. However, the problem of the mechanism of the electrodeposition of filled systems containing water-soluble film-forming agents has been very little studied. Previously it was assumed that the electrodeposition of pigments obeys the rules governing the electrophoretic deposition of dispersions, although this was not confirmed experimentally. The existing ideas about the mechanism of the electrophoretic deposition of dispersions are applicable to lyophobic colloids stabilised by an ionic mechanism. They are based on Deryagin and Landau's theory of the stability and coagulation of lyophobic colloids, which at its present stage of development takes into account not only pair but also collective interactions of the species, the possibility of their fixation at long distances from one another, as well as the influence of homogeneous and inhomogeneous electric fields[59-68].

The systems of water-soluble lacquer materials considered here differ from the systems of lyophobic colloids stabilised by an ionic mechanism primarily by the fact that the concentration of the third component, constituting, together with the aqueous dispersion medium, a single phase, is very high compared with the concentration of the disperse phase. In fact, one is dealing with dispersions of pigments in a concentrated aqueous solution of a polyelectrolyte. The problems of the stability, electrokinetic properties, and electrodeposition of such systems have already been examined[69-72].

1. Interaction of Water-Soluble Film-Forming Agents with Pigments

Since in the absence of a film-forming agent there is no electrodeposition of the majority of pigments from a pigment–water system on electrodes[73,74], it was concluded that the pigment particles in an aqueous medium are surrounded by particles of the binder, which impart to them a negative charge[74-76] and are responsible for their electrodeposition[74-77].

The interaction of water-soluble film-forming agents with pigments was studied in relation to the Printex U carbon black and R-820 titanium dioxide, which are used in electrodeposition systems[69]. The determination of the ξ-potential of the particles and of the sedimentation potential on a Figurovskii balance demonstrated the stabilising influence of film-forming agents in relation to pigments. It has been established on the basis of the surface tension isotherm of an aqueous solution of rezidrol in the presence of pigments that a considerable degree of

adsorption is characteristic of the test systems. In order to determine its nature, a study was made by a gravimetric method of the adsorption of rezidrol on the test pigments from aqueous solutions at different concentrations with subsequent removal by washing; the results were used to calculate the adsorption parameters. It was established that part of the adsorbed film-forming agent is bound to the surface of the pigment by irreversible linkages. Thus in real electrodeposition systems the pigment is stabilised by a binder adsorbed on its surface. This condition is necessary for the electrodeposition of the pigment on the anode, which has been demonstrated by the absence of the electrodeposition of oxidised carbon black from an aqueous medium. In this case the carbon black–water system has a high kinetic stability and a high ξ-potential of the particles (62 mV); nevertheless in an electric field the carbon black particles are not deposited on the anode.

Thus the deposition of pigments on the anode is determined by the film-forming agent linked to their surface by adsorption interaction.

2. The Nature of the Stability of Dispersion of Pigments in Solutions of Water-Soluble Film-Forming Agents

In order to elucidate the nature of the stability of the systems under consideration, a study was made of their aggregative and kinetic stability as a function of the ξ-potential of their particles[69]; the ξ-potential was varied by introducing into the system a 20% NaCl solution, which influences the thickness of the electrical double layer but does not lead to the loss of solubility of the film-forming agent, and also by changing the pH of the medium within the limits where the film-forming agent is soluble. Despite the fact that the ξ-potential was changed almost by a factor of two, neither the optical density of the systems nor the volume and weight of the sedimentation deposit were changed. Consequently the aggregative and kinetic stabilities of the dispersions are not affected by a change in the ξ-potential.

The data quoted show that, apart from the ionic-electrostatic factor, the non-electrostatic stability factor plays an important role in the mechanism of the stabilisation of the particles. This is demonstrated by the finding that, when the concentration of the film-forming agent in solution diminishes appreciable (to a value less than that required for the complete adsorption saturation, calculated as 15 mg of rezidrol per gram of TiO_2), the ionic-electrostatic stability factor becomes of decisive importance in the stabilisation mechanism[67,71]. An analogous conclusion was also reached in a study[78] devoted to colloidal chemical interaction of titanium dioxide with water-soluble acrylic copolymers.

3. The Study of the Electrodeposition of Pigments on the Anode

The electrodeposition of pigments on the anode has been examined[71] in relation to the rezidrol–titanium dioxide system. The influence of the electrodeposition parameters on the variation of the amount of the electrodeposited pigment on the anode is analogous to the influence of the deposition parameters on the yield of the deposit on the anode for a non-pigmented solution of a film-forming agent, which indicates the decisive role of the latter in the pigment electrodeposition mechanism. The coagulation thresholds for the test systems of filled carboxyl-containing polyelectrolytes virtually correspond to the concentration of the precipitant causing the precipitation of a deposit from a solution of an unfilled film-forming agent.

However, there is also a weak variation of the yield of the pigment deposit on the anode with the ξ-potential of the particles. One may therefore conclude that electrophoresis may be important in the mechanism of the concentration of pigment particles in the layer near the anode. This factor explains the enrichment of the electrodeposited film in the pigment compared with the pigment concentration in the bath. An electrid field does not influence the optical densities of the systems; consequently, there is no structure formation in the test systems in an electric field. The dimensions of the pigment aggregates in the coatings obtained by the pouring and electrodeposition methods are the same. The attempt to apply quantitative electrophoretic relations to the calculation of the amount of electrodeposited pigment on the anode gave rise to more than an order of magnitude discrepancy between the experimental and calculated results.

Evidently the phenomena under consideration are caused by the fact that the non-electrostatic stability factor plays an appreciable role in the mechanism of the particle stabilisation in the test systems; consequently, the theory of the electrophoretic formation of deposits on the anode, developed for systems stabilised by an ionic mechanism, cannot be applied to the case under consideration[79]. The deposition of pigments on the anode is due to the loss of solubility in the anodic compartment by the water-soluble film forming-agent adsorbed on the surface of the pigments. On the other hand, if the stability of the dispersions is caused mainly by the electrostatic factor (the TiO_2–0.02% rezidrol solution system), structure formation does take place in an electric field. In this case the determination of the yield of the pigment on the anode as a function of the duration of the electrodeposition gives results closer to data calculated in accordance with the electrophoretic mechanism[71,72].

4. The Influence of Pigments on the Parameters of the Electrodeposition Process

There are data, albeit contradictory, showing that pigments can influence the thickness and the electrical resistance of the anodic deposit and hence also the electrodeposition parameters[74,80]. The influence of the Printex U carbon black and titanium dioxide (R-820) on the electrodeposition process has been studied at constant currents and potentials in relation to rezidrol[72]. The results were compared with the structural-mechanical properties of non-hardened coatings obtained from the rate of development of the shear deformation between two plane-parallel plates, and also with the viscosities and electrical conductivities of the systems used for electrodeposition. It was established that the influence of the pigments on the electrodeposition parameters depends on their influence on the rheological properties of the electrodeposited system and the resulting coatings and also on the ability of the pigments to form conducting structures in a system with a film-forming agent. Thus the data presented confirm the validity of the hypothesis that the electrodeposition of pigments on the anode takes place as a result of the loss of solubility, in the layer near

the anode, by the film-forming agent linked to the surface of the pigments by adsorption interaction.

IV. THE INFLUENCE OF ELECTRODEPOSITION CONDITIONS ON THE FORMATION OF A DEPOSIT ON THE ANODE AND THE PROPERTIES OF THE COATINGS

Apart from the composition of the lacquer system, the electrodeposition of water-soluble lacquer materials and the properties of the resulting coatings are known to be greatly influenced by the concentration and pH of the lacquer material in the bath, the electrical parameters, the process time, temperature, and rate of stirring[7,13,14,73,81]. The form of the rectified current has been found to have an influence in a number of investigations[82-84]. Coatings with optimum properties are produced in a specific range of values of the parameters enumerated. The causes of the influence of the deposition parameters on the electrodeposition process and the properties of the coatings have been investigated[85-87].

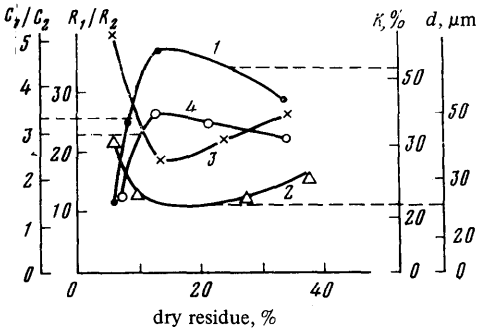


Figure 6. Dependence of the scattering capacity of the bath K (curve *1*), the thickness of the coatings d (curve *2*), and the ratios of the capacitative (C) (curve *3*) and ohmic (R) (curve *4*) components of the impedance obtained at frequencies of 500 Hz (R_1, C_1) and 20 000 Hz (R_2, C_2) on the rezidrol concentration in the bath[85].

1. The Influence of the Concentration of the Lacquer Material in the Bath

The dependence of the protective properties of coatings and of the scattering capacity of the bath on concentration is illustrated in Fig. 6. The maximum scattering capacity of the bath corresponds to the most effective corrosion-protective properties of the coatings characterised by the capacitative–ohmic method[88].

Electron microscope studies of the structure of the coatings showed that structural elements of smallest size are then close-packed to the maximum extent. At a rezidrol concentration smaller or greater than the optimum value, the coatings have a structure with loose packing.

It has been shown[85] that the influence of the concentration of the aqueous solution on the electrodeposition process and the structure and properties of the resulting coatings is associated with the difference between the supermolecular structures of the solutions of the film-forming agents. The study of the viscosities and conductivities of these solutions showed that at elevated concentrations, where the resistance of the anode diminishes, the protective properties of the coatings become less effective, and defects such as bulges arise, structure formation processes begin in the test solutions. This results in an increase of the mass of each structural element of the solution involved in the interaction with hydrogen ions, which leads to the formation of thickened coatings with bulges. Under these conditions, the number of carboxylate ions on the surface of each structural element involved in the neutralisation processes diminishes, as shown by the shift of the inflections on the conductimetric titration curves towards lower pH values. Under the conditions of a structured solution, the deposition of the same mass of polymer as at lower concentrations therefore requires a smaller number of hydrogen ions. This results in an increased acidity in the anodic compartment, which leads to an increase of the solubility of the anode, the expansion of the diffusion layer in the anodic compartment where deposition takes place, and the formation of thickened coatings with a loose packing of the structural elements.

If the electrodeposition is carried out in a structured solution with reduced electrical parameters (i.e. the concentration of hydrogen ions formed in the anodic compartment during the electrolysis of water is diminished), then it is possible to avoid the above defects to a large extent. In electrodeposition in the region of reduced concentrations of the film-forming agent in the anodic compartment there is apparently also an excess of free hydrogen ions owing to the low concentration of the ions of the film-forming agent. The reaction zone therefore expands, which results in the formation of loose bulky deposits and the solubility of the anode increases owing to the increased acidity of the solution in the anodic compartment.

The electrodeposition of low-resistance film-forming agents has characteristic features due to the poor structural-mechanical properties of their deposits. In the region of concentrations where structure formation takes place in the solution, a decrease and not an increase in the weight of the coating is observed during delectrodeposition. This is apparently caused by the slipping of the deposit from the anode under the influence of its own weight owing to its poor structural-mechanical properties. Such slipping can be observed visually. It entails the formation of bulges and runs on the coating.

2. The Influence of the Electrical Parameters and Process Time

With increase of the potential and current and also process time, an increase in the weight of the coating is initially observed in accordance with a virtually linear law, the growth of the thickness of the coating then slows down, and, on further increase of the electrical parameters and process time beyond certain limiting values, "superdeposition" defects are observed on the coatings, manifested by bulges and a "shagreen" effect; for low-resistance lacquer materials, a decrease in the weight increment of the coatings is observed.

The maximum packing density and the most effective protective properties of the coatings correspond to the optimum electrical parameters and process time. With increase of time, potential, and current above the optimum values, coatings are formed which consist of

aggregates of indefinite form and with a loose packing. Direct measurement of the temperature of the anode established[86] that the above phenomena are caused by the increased evolution of heat with increase of the above parameters. The decrease of the quality of the rezidrol coatings described above is observed when the temperature of the anode exceeds 60°C, the reaction time is 2 min, and the potential is 200 V. The impairment of the quality of the coatings is altogether absent in electrodeposition on a cooled anode whose temperature does not exceed 30°C, at a potential up to 300 V, and for a process time up to 5 min. It has been shown that, with increase of the temperature of the anode, there is an appreciable increase of the rate of formation of a deposit on the latter, which impairs the structure and protective properties of the coatings.

In the electrodeposition of low-resistance lacquer materials an increase of the electrical parameters and process time entails an increase of the rate of electrodeposition and of the thickness of the coatings, which is followed by their decrease owing to the poor structural-mechanical properties of the deposits, the latter becoming still more inferior when the temperature increases.

3. The Degree of Neutralisation of the Binder and the Type of Neutraliser

The solubility in water of film-forming agents used for electrodeposition is ensured by the neutralisation of carboxy-groups by bases. Electrodeposition takes place in an alkaline medium. The pH of the lacquer material has a significant influence on the stability of the lacquer system, the rate of electrodeposition, and the quality of the coatings in electrodeposition. As a rule, for each lacquer material there is an optimum pH range. The existence of a lower pH limit is due to the stability of the water-soluble film forming-agents whose acid form is insoluble in water. An increase of pH entails an increased degree of neutralisation of the carboxy-groups of the film-forming agent and an increase in the charge per unit molecular weight (owing to the increase of the degree of dissociation). This is accompanied by an increased repulsion of like charges and an increased solubility of the film-forming agent in water. In a highly alkaline medium an aqueous system is so stable that the formation of coatings by electrodeposition is hindered[73,77,81].

The thickness of the electrodeposition coatings therefore increases with increasing pH of the system and the curve relating the scattering capacity of the solution in the bath and the protective properties of the coatings to the pH passes through a maximum. The presence of the latter is caused, on the one hand, by the decrease of the size of the structural elements of the solution with increasing pH and by the increase of the packing density in the structure of the coatings and, on the other hand, by a significant decrease of the thickness of the coatings.

There is information showing that not only the pH but also the type of neutraliser used to convert the film-forming agent into a water-soluble state can influence the electrodeposition process[89-92]. In order to render the film-forming agent water-soluble, different neutralisers are employed: ammonia, primary, secondary, and tertiary alkylamines, hydroxyalkylamines (aminoalcohols), and morpholine; inorganic alkalies (KOH, NaOH) are sometimes used. The influence of the type of neutraliser on the electrodeposition process has been investigated[93] in relation to rezidrol. The following neutralisers were used: ammonia, triethylamine (TEA), triethanolamine (TEOLA), and diethylenetriamine (DETA). It was established that, in the neutralisation of polyacids by diethylenetriamine, conformational transformations take place in the system, associated with the partial "twisting" of the macromolecules and with processes involving partial conversion into a globular form. The reason is that the composition of DETA includes two primary amino-groups and one secondary amino-group. As a result, the film-forming agent forms amide linkages with two primary DETA amino-groups and the remaining free carboxy-groups interact with the secondary amino-groups of the neutraliser. The coatings formed in electrodeposition from globular solutions exhibit a reduced capacity for relaxation processes. Consequently, owing to the increase in the polarisation component, there is an appreciable increase of the resistance of the anode, which permits electrodeposition at higher potentials. As a result, DETA can be recommended as an additive to the electrodeposition bath in order to increase the potential, which makes it possible to increase the scattering capacity of the bath[94].

4. The Influence of Deposition Parameters on the Physicomechanical Properties of the Coatings and the Molecular Weight of the Section of the Chain between the Effective Nodes of the Three-Dimensional Network

The influence of the above electrodeposition parameters on the physicomechanical properties of coatings and the quantity M_c has been studied[95] in relation to rezidrol. In order to estimate the physicomechanical properties of the coatings as a function of the deposition conditions, a generalised parameter, namely the resistance to wear, was adopted as a criterion. The rupturing force for coatings electrodeposited on aluminium foil was also determined as a function of the deposition parameters—from the difference between the strength of the coating—foil system and the strength of the foil without the coating. It was established that coatings with the optimum mechanical properties are formed for the same electrodeposition parameters as in the formation of coatings with the optimum protective properties and with the maximum scattering capacity of the system, i.e. under conditions where the formation of a coating whose structure consists of elements of the smallest size is most uniform and is most close-packed. At the same time, M_c (according to equilibrium swelling data) for coatings formed for different electrodeposition parameters changes only slightly, but the minimum value of M_c corresponds to the coating produced for the optimum parameters. All these findings suggest that, as the electrodeposition parameters are changed, the chemical bonds within and between structural elements of the coating are redistributed.

5. The Influence of Hydrodynamic Conditions in the Bath on the Electrodeposition Process

The electrodeposition of water-miscible lacquer materials takes place with constant stirring whose optimum rate depends primarily on the lacquer material employed; usually the optimum rate of stirring is chosen empirically. There are data[24-26,96,97] showing that the hydrodynamic conditions in the bath (i.e. the rate of stirring) influence the thickness of the electrodeposited coating. It has been shown[24] in relation to the electrodeposition of acrylic

lacquer on a rotating disc electrode that there is a definite (limiting) rate of rotation of the disc electrode above which a deposit is not formed. The authors explain this phenomenon by the decreased thickness of the diffuse component of the electrical double layer and hence by the decreased number of hydrogen ions required for the formation of a deposit.

The influence of the rate of stirring of the lacquer material on the rate of electrodeposition, the thickness and protective properties of coatings, and the relation between the rate of stirring and the electrodeposition parameters has been investigated[7] for the FL-093 primer and the FL-149E enamel. For both lacquer materials, there is a sharp decrease of the rate of electrodeposition with increasing rate of stirring and its extent is the same. This is because, with increase of the rate of stirring, there is the same decrease in the thickness of the diffuse layer of hydrogen ions produced in the electrolysis of water and responsible for the formation of the deposit. However, the maximum rate of stirring at which the coating is not formed is higher for the FL-093 primer, which is probably associated with the higher conventional current yield, i.e. with the higher rate of the electrodeposition in the absence of stirring compared with the FL-149E enamel. The increase of the optimum range of electrical parameters and of the deposition time with increasing rate of stirring has been established by the capacitative-optical method. Direct measurement of the temperature of the anode by means of a Chromel–Copel thermocouple showed that this is caused by the decreased temperature of the anode with increasing rate of stirring, which is related to the influence of the rate of stirring on the heat transfer in the system.

Since the scattering capacity of the bath in colouring by electrodeposition is proportional to electrical parameters, it can be increased by creating a special stirring system in the bath.

6. The Influence of the Pulsation of the Rectified Current on the Electrodeposition Process

The electrodeposition of water-miscible lacquer materials requires the use of a rectified current. The coloured layers obtained at a constant potential and at a constant current density are distinguished in terms of the mode of supply of the electric current. There have been a number of studies and patents[82–84,98,99] devoted to the problems of the selection of schemes for the supply of the electric current in electrodeposition. In particular, there is information showing that with a pulsed supply of the current an increase in the thickness of the electrodeposited coatings is observed in some cases[98]. The influence of the form of the rectified current on the electrodeposition process under the conditions of a constant potential has been investigated[86]. It has been established that the influence is associated with the differences in the thermal phenomena on the anode when different schemes for the rectification of the current are used. An increase of the amplitude of the pulsations for the same effective rectified current leads to greater heating of the anode largely owing to the change of the maximum rectified current. In the single-phase half-wave rectification, a current passes through the bath during one half-period, its amplitude exceeding almost by a factor of three the effective value. This probably leads to an increase of the amount of heat evolved during a time shorter than one half-period. Owing to the low thermal conductivity of the film, the heat evolved gradually accumulates in the deposited layer and the temperature of the anode continues to increase. The increase of the temperature of the anode increases the rate of electrodeposition. This results in the formation of thicker coatings (or, in the case of low-resistance lacquer materials, thinner coatings owing to the slipping of the film from the anode because of its poor structural-mechanical properties), but the scattering capacity of the bath decreases and the protective properties of the coatings become less effective. Hence the pulsed supply of the current is desirable only in the electrodeposition of film-forming agents with a high rigidity.

Thus the mechanism of the process involving the formation of polymer coatings, developed in the last 10–15 years[100–104], operates also in the formation of films from water-miscible lacquer materials by electrodeposition. Under these conditions, the polymer coating is produced from the structure arising in the anodic compartment before the start of the thermal hardening process when the oligomer loses its solubility in water; the deposit is formed on the anode owing to the interaction with the hydrogen or metal ions formed as a result of the accompanying electrochemical reactions in the aqueous medium at the anode.

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