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VARIOUS TECHNOLOGICAL  
PROCESSES

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## Electrodeposited Paint-and-Varnish Nickel–Polymer Coatings

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**Abstract**—Specific features of preparation of paint-and-varnish nickel–polymer coatings by joint cathodic electrodeposition of an amine-containing oligomeric electrolyte and nickel were studied. The coatings obtained exhibit layer-by-layer heterogeneity, with the lowest layer constituted by an intermetallic compound of nickel with iron. The coatings are characterized by higher degree of cross-linking compared to the polymer coatings without nickel. A paint-and-varnish formulation based on a nickel–polymer film-forming agent was developed for electrodeposition of corrosion- and wear-resistant coatings.

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Metallopolymers are heterogeneous systems based on polymers and finely dispersed metal particles bound to them by adsorption. These materials combine the advantages of polymers (low density, high elasticity and strength) with the electrical conductivity and magnetic, antifriction, and other properties characteristic of metals [1]. Deposition of metal–polymer coatings is of particular interest. Up to now, the most widely used procedure for deposition of such coatings was the electrophoretic-electrochemical procedure combining the electrochemical procedure for deposition of metal coatings with electrophoresis of polymer particles cation-stabilized with surfactants [2–4]. In this case, the metal is the coating matrix. Despite good properties of the coatings obtained, this procedure has a drawback associated with difficult bath adjustment caused by insufficient stability of ion-stabilized polymer particles in an electric field and, correspondingly, with low throwing power of the system, typical of electrophoretic deposition. Therefore, a combination of the electrodeposition of polymeric electrolytes with metal electroplating is suggested as a procedure for deposition a paint-and-varnish metal–polymer coating.

This approach will allow the above drawbacks in deposition of coatings to be eliminated.

Water-soluble polymeric film-forming electrolytes are used as binders for paint-and-varnish systems intended for painting by electrodeposition, a method widely used in industry for more than 50 years for preparing priming and single-layer coatings on a metal surface [5, 6]. The method is based on the capability of polyelectrolytes to change the solubility with variation of pH of the medium. The main electrochemical process in electrodeposition of polymeric electrolytes is water electrolysis, resulting in alkalization of the near-cathode layer and acidification of the near-anode layer. Correspondingly, carboxyl-containing polymeric electrolytes converted into the water-soluble state by reaction with organic amines lose their solubility and are electrodeposited on the anode, whereas amine-containing polyelectrolytes dissociating in acid solutions lose solubility in an alkaline medium of the near-cathode layer and are electrodeposited on the cathode.

Because this procedure for coating deposition is technologically similar to electroplating processes based on electrolytic reduction of metals on the cathode,

it seems possible to perform electrodeposition of an amine-containing polyelectrolyte on a cathode jointly with electrolytic reduction of metals from their salts. An attractive feature of such approach is that cathodic deposits of metals deposited in the presence of polymers and surfactants form nanosized metal sols [7]. Specifically such conditions are created in the near-electrode layer at joint electrodeposition of polyelectrolytes and metal salts. This should be manifested in the structure and properties of the coatings.

The possibility of depositing metal–polymer coatings with a polymer-based matrix by this procedure was demonstrated by the example of nickel–polymer coatings [8], and the optimum formulation and optimum electrodeposition conditions were found. It was found that nickel–polymer coatings exhibit increased corrosion resistance, several times higher than that of paint-and-varnish coatings based on the initial polymer system. High levels of the elasticity and strength with significant enhancement of the coating hardness also appeared to be untypical. Nixed nickel–polymer electrolyte exhibits high throwing power and is aggregatively and kinetically stable. From the thermodynamic viewpoint, polyelectrolyte solutions are single-phase systems.

This study deals with specific features of the preparation of composite nickel–polymer coatings by joint electrodeposition of a polyelectrolyte with the metal on the cathode and with the use of the nickel–polymer film-forming agent in the paint-and-varnish formulation for electrodeposition painting.

## EXPERIMENTAL

As polymeric electrolyte we used film-forming agents of the commercial paint-and-varnish material for cathodic electrodeposition (analogs: Cathogard W 781309 produced by BASF and GEN 6W 780/973 produced by PPG), namely, an epoxy–amine adduct modified with blocked isocyanate and converted into water-soluble state by reaction with acetic acid. The gravimetric concentration of the polymeric electrolyte in the aqueous solution is 32–35% counting on the dry residue, and the mean molecular mass of the polymeric electrolyte is 900–1200. The formation of the polymer coating on the cathode is associated with the regeneration of the amino groups of the polyelectrolyte in the alkaline medium of the near-cathode layer. The subsequent thermal curing at 180°C leads to the

formation of coatings owing to chemical reaction of the deblocked isocyanate groups with hydroxy and amino groups.

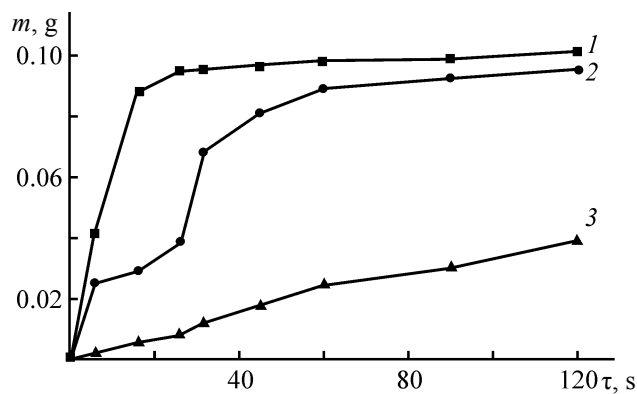
As the metal for preparing the metal–polymer coating, we chose nickel, because it is characterized by stability in acid and alkaline solutions. We used for electroplating nickel acetate in the form of an 80 g L<sup>-1</sup> aqueous solution. To prepare the combined electrolyte, we chose the polyelectrolyte concentration of 10–16% counting on the dry residue and the nickel acetate concentration corresponding to 10 : 1 ratio of polyelectrolyte and nickel acetate [8].

Joint electrodeposition was performed in a laboratory installation for electrodeposition painting in a 1-L bath. Insoluble 08Cr10Ni20Ti2 (AISI 303) stainless steel anode was used in electrodeposition of polyelectrolyte-based systems. Because the coating matrix is the polymer, the electrodeposition conditions were made maximum similar to those of the polyelectrolyte electrodeposition. Electrodeposition was performed at a constant voltage in the interval 120–240 V at 27–32°C for 60–180 s. Metal plates made of 08KP steel (AISI A 622) of 0.2 dm<sup>2</sup> area, degreased and pretreated in accordance with ISO 1513:2010 requirements, served as cathodes. Thermal curing of the coatings was performed at 180°C for 20 min. Under these conditions, even flawless coatings meeting the ISO 4628 [GOST (State Standard) R 51691–2008) requirements in the external appearance were obtained.

For measuring the coating thickness, adhesion, bending strength, and impact resistance and for performing accelerated corrosion tests, we used standard procedures accepted in paint-and-varnish and electroplating technologies. The characteristics of the nickel–polymer coating obtained were compared to those of the coating prepared from the pure electrolyte under standard electrodeposition conditions.

The degree of cross-linking of the coatings was judged from data on the determination of the sol and gel fractions in a Soxhlet apparatus and from the results of calculating the molecular mass of the chain segment between the cross-linking points,  $M_c$ , from the data on equilibrium swelling in vapor of a chosen thermodynamically active solvent, in accordance with the Flory–Rehner theory.

The elemental composition of the coatings was determined by energy-dispersive X-ray analysis with a Quanta 650 device equipped with an EDAX unit.



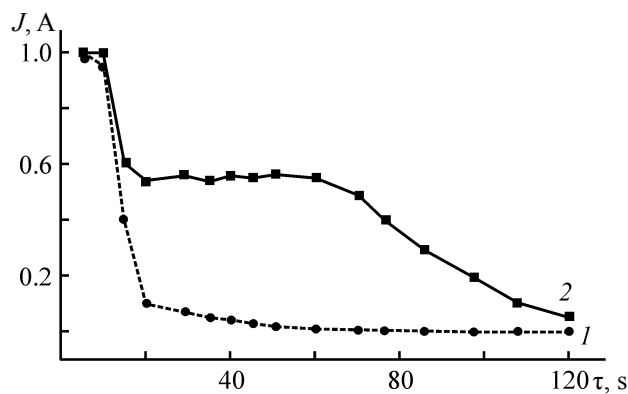
**Fig. 1.** Weight  $m$  of electrodeposited coatings as a function of the electrodeposition time  $\tau$ . Coating: (1) polymer, (2) nickel-polymer, and (3) nickel.

The occurrence of chemical reactions between the components in the course of the coating formation was judged from the DSC data obtained with a Q-100 device at a heating rate of 5 deg min<sup>-1</sup> in an argon atmosphere in the temperature interval 20–150°C.

The crystal structure of the metal phase of the coatings was studied by X-ray diffraction with a DRON-2 powder diffractometer with special collimation of the primary and diffracted beams in the reflection mode in the angle range  $2\theta = 40^\circ\text{--}90^\circ$  (CuK $\alpha$ ,  $\lambda = 0.154$  nm, Ni filter).

## RESULTS AND DISCUSSION

The deposition of metal-polymer coatings is a combination of the physicochemical mechanisms of the electrodeposition of polymeric electrolytes and metals, although the characteristics of their individual electrodeposition are different. For example, electrodeposition of polyelectrolytes occurs at high voltage and low current, whereas the deposition of metals, on the contrary, requires relatively low voltage and high current. The times in which the acceptable coating thickness is reached differ by an order of magnitude. For example, the calculated electrodeposition equivalents (mg C<sup>-1</sup>) obtained at  $i = \text{const} = 1$  A dm<sup>-2</sup> are 7.8 for the nickel-polymer coating, 16 for the polymer coating, and 0.3 for nickel from nickel acetate. As can be seen, the polymer coating is electrodeposited at a considerably higher rate compared to the nickel coating whose formation rate is controlled by electrochemical reduction of nickel on the cathode. Introduction of a nickel component into the combined



**Fig. 2.** Current  $J$  as a function of electrodeposition time  $\tau$  (“current curve”) for the deposition from (1) polymeric and (2) mixed nickel-polymer electrolytes.

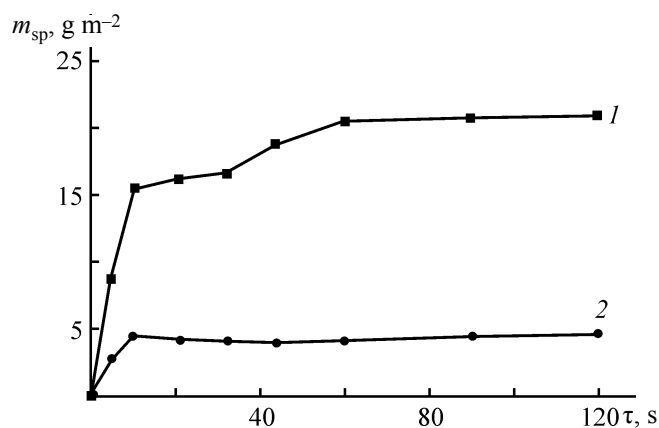
nickel-polymer electrolyte leads to the average value of electrodeposition rate of the metal-polymer coating.

Figure 1 shows how the weight of the nickel-polymer coating depends on the electrodeposition time at  $U = \text{const} = 200$  V.

As seen from Fig. 1, in the initial period, in the time interval 10–45 s, the  $m = f(\tau)$  curve for the nickel-polymer coating (2) has a step, which is untypical of electrodeposition of polymeric electrolytes. This may be due to the initial predominant deposition of nickel and evolution of hydrogen. After that, the curve acquires a typical shape for electrodeposition of polymeric electrolytes. This fact suggests layer-by-layer deposition of the metallic and polymeric components in the course of formation of the nickel-polymer coating, with the lower layer adjacent to the metal support enriched in nickel.

The dependence of the current on the electrodeposition time (“current curve”) for the polymeric and mixed nickel-polymer electrolytes is shown in Fig. 2.

As can be seen, in deposition of the nickel-polymer coating, the current curve changes essentially compared to the electrodeposition of the pure polymer. In polyelectrolyte electrodeposition, the current rapidly decreases because of the formation of the polymer deposit insulating the electrode. In deposition of the nickel-polymer coating, a complex pattern is observed. In the initial period, apparently, predominant deposition of nickel is observed; it is followed by joint electrodeposition of the polymer with nickel, and the curve acquires the traditional shape. Such a complex current curve suggests the nickel deposition in the initial

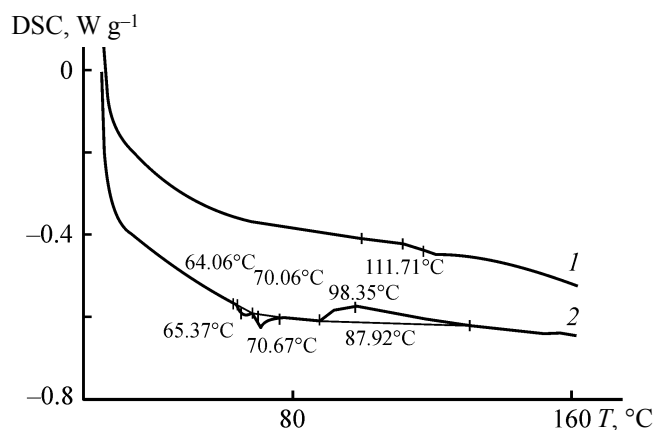


**Fig. 3.** Coating weight per unit surface area  $m_{sp}$  as a function of deposition time  $\tau$ . (1) Coating before extraction and (2) deposit after extraction.

period and the possible formation of a coating with layer-by-layer heterogeneity.

To determine the layer-by-layer composition of the nickel-polymer coating, we examined 24 coating samples obtained by interrupting at 5-s intervals the electrodeposition process (overall time 120 s), keeping the other parameters equal. The uncured coatings obtained were subjected to solvent extraction in a Soxhlet apparatus. The solvent choice was made using a “blank sample,” i.e., the experiment was performed with a polyelectrolyte solution without nickel-containing component. As solvent we chose acetone, in which the polymeric deposit on the support completely dissolves. We proceeded from the assumption that the insoluble part of the electrodeposited material is electroplated metal. If the nickel component of the mixed nickel-polymer electrolyte is deposited only in the initial time period, the content of the insoluble fraction will be equal for all the samples taken 10–20 s after the start of the electrodeposition. Indeed, the weight of the residual fraction of the metal-polymer coating after the extraction with acetone in the samples obtained at different electrodeposition times starting from 20 s is approximately constant and fluctuates about 30%. The results were confirmed by averaging over five samples. The results are shown in Fig. 3.

The obtained data on the percent content of the insoluble fraction contradict the data on determination of the elemental composition of the nickel-polymer coating by energy-dispersive X-ray analysis. As found by this method, the nickel-polymer coating contains

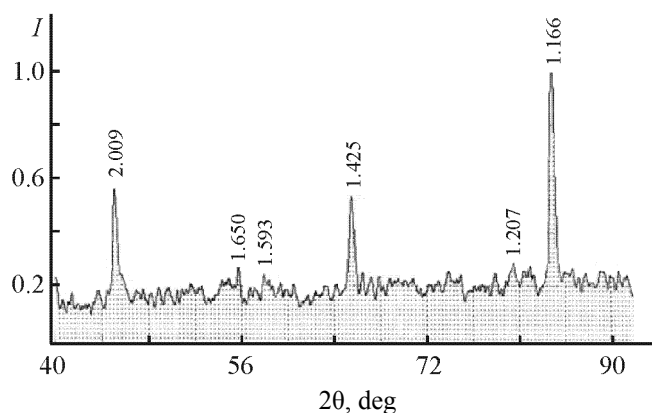


**Fig. 4.** DSC curves of (1) polymer and (2) nickel-polymer coatings. ( $T$ ) Temperature.

about 4–6% nickel metal and 8–6% iron [8], which is inconsistent with the extraction results.

We attributed this result to the fact that the insoluble fraction of the uncured coating could contain, along with the metal, the gel of the three-dimensional insoluble polymer formed before the start of the thermal curing. This assumption is indirectly supported by data on determining the content of sol and gel fractions in the cured coatings and the mean molecular mass of the chain segment, calculated in accordance with the Flory-Rehner theory.

As we found, the gel fraction content of the nickel-polymer coating, 86%, considerably exceeds the value obtained for the pure polymer coating, 67%. As determined by equilibrium swelling in the chosen thermodynamically active solvent, butyl Cellosolve, the mean molecular mass of the chain segment between cross-linking points is 975.5  $\text{g mol}^{-1}$  for the polymer coating and 358.2  $\text{g mol}^{-1}$  for the nickel-polymer coating. Thus, the degree of cross-linking of the nickel-polymer coating, compared to the polymer coating, increased by a factor of 3. The higher is the mean molecular mass of the segment between the cross-linking points, the looser is the network. Hence, the network of the polymer coating is looser than that of the nickel-polymer coating. All these facts suggest possible formation of a three-dimensional network in metal-polymer coatings before the start of thermal curing. As a result, the relative content of the nickel-polymer coating fraction insoluble in the course of extraction increases. We attributed this result to the catalytic properties of nickel. This is proved by the DSC data. We monitored the thermal curing of



**Fig. 5.** Diffraction pattern of the nickel–polymer coating. (*I*) Reduced intensity and ( $2\theta$ ) Bragg angle.

the coatings obtained by electrodeposition from the polyelectrolyte without nickel (curve 1) and with nickel (curve 2). The DSC data are shown in Fig. 4.

As can be seen, in the case of the nickel–polymer coating there is an exothermic peak localized in the range 98–120°C, which is considerably lower than the temperature of the formation of the three-dimensional network. This result may be due both to the catalytic action of nickel on the curing of the amine-containing oligomer and to the direct interaction of the oligomer with the surface of nickel particles, revealed previously [8], as these particles at the moment of deposition on the cathode exhibit high reactivity owing to their nanometric size [7]. To refine these assumptions, we studied the coatings by Fourier transform IR spectrometry. The results obtained show that the spectra of the cured nickel–polymer and polymer coatings are essentially

**Table 1.** Parameters of the pigmented nickel–polymer formulation

Electrodeposition parameter	Value
pH	5.6–5.8
Specific electrical conductivity, $\mu\text{S cm}^{-1}$	3350–3480
Dry residue (d.r.), %	16.5–17.2
Ratio of pigment to nickel–polymer (counting on d.r.)	6:1– 6.5:1
Working solution temperature, °C	28–32
Process voltage, V	180–200
Deposition time, s	120

similar, except the range 420–440  $\text{cm}^{-1}$ , which can be assigned to Ni–C bounds formed by chemisorption interaction of nickel with the polyelectrolyte. Thus, we assumed that the chemisorption contributes to the formation of the three-dimensional network of the metal–polymer coating, resulting in the formation of the three-dimensional cross-linked structure in the course of coating formation on the support. This process is responsible for the increased content of the insoluble fraction in extraction of the electrodeposited material.

The X-ray diffraction data confirm the presence of a metal layer in the nickel–polymer coating. The diffraction pattern of this layer at the exposure of 0.15 and maximum intensity of 154 is shown in Fig. 5.

The calculations show that the nickel–polymer coating contains not pure nickel but a nickel–iron intermetallic compound. The diffraction pattern completely corresponds to that of the known MountJoy meteorite (Pennsylvania, the United States, 1887). The metal–polymer coating has cubic unit cell ( $1\text{m}^3\text{mc}$ ) with the parameter  $a = 2.868 \text{ \AA}$ . Like the meteorite, it has the structure consisting of four parallel differently oriented kamacite plates and interlayers consisting of taenite against the background of a finely grained mixture of kamacite and taenite. This structure has not yet been reproduced on the Earth. Of course, this fact of surprising structure of the intermetallic compound formed under the conditions of joint electrodeposition of nickel and polyelectrolyte on the cathode requires additional studies.

To elucidate the causes of the formation of the iron–nickel intermetallic compounds, we assumed the possibility of the dissolution of the cathode (carbon steel) in the acidic solution. The possibility of the dissolution of an iron cathode under the conditions of cathodic polarization is recognized by electrochemists [9]. Large amount of iron was also found in polymer coatings obtained on a steel support by cathodic electrodeposition [5, 6]. The absence of iron originating from the anode dissolution was confirmed by X-ray diffraction analysis of coatings that we obtained on nonferrous metal (brass, copper, aluminum) supports. The formation of the intermetallic compound may be due to partial dissolution of iron in the acidic medium of the electrolyte and occupation of the resulting vacancies by nickel atoms.

Thus, the composite nickel–polymer coating that we obtained exhibits, in our opinion, layer-by-layer heterogeneity and has the following structure: iron–

**Table 2.** Properties of nickel–polymer and polymer paint-and-varnish coatings

Property	Pigmented polymer coating	Pigmented nickel–polymer coating
Thickness [GOST (State Standard) R 51694–2000 (ISO 2808–97), $\mu\text{m}$ ]	20–22	23–25
Adhesion (GOST 15140/ISO 2409/ASDM D 3359), points	1/0/5B	1/0/5B
Bending strength [GOST R 52740–2007 (ISO 1519:2002)], mm	2	1
Impact resistance [(GOST R 53007–2008 (ISO 6272-1:2002)], kg s cm <sup>-1</sup>	70	100
Hardness [GOST R 54586-2011 (ISO 15184:1998)], arb. units	3H	7H
Salt resistance in a neutral salt mist chamber [GOST 9.905–2007 (ISO 9227, ASTM B 117), h]	1200	1850
Wear resistance, specific wear (GOST 20811–75), g $\mu\text{m}^{-1}$	1540	3100

nickel intermetallic compound; nickel-containing polymer layer; pure polymer.

For practical use, we developed a black paint-and-varnish formulation based on the nickel–polymer compound and studied its properties. The optimum parameters of the formulation allowing preparation of flawless continuous coatings 23–25  $\mu\text{m}$  thick are given in Table 1.

We determined the properties of nickel–polymer coatings in comparison with the polymer coatings obtained from the same polyelectrolyte under standard conditions (Table 2).

As can be seen, as compared to coatings based on the paint-and-varnish system without nickel, the coatings based on the nickel–polymer film-forming agent, having the same adhesion, exhibit significantly higher levels of hardness and strength, high elasticity, better protecting properties, and higher wear resistance. Preservation of the high elasticity of the coatings may be due to the formation of fractal clusters in the polymer matrix, formed in the course of electrodeposition of metal nanoparticles in the near-electrode layer. The morphology of nickel–polymer coatings was studied previously [8]. High corrosion-protecting properties of the nickel–polymer coating can be accounted for by the formation of the iron–nickel intermetallic compound (“meteorite coating”) in the coating.

The paint-and-varnish formulation that we developed was used instead of polymer and nickel coatings for painting an experimental batch of casings for stators and rotors of micromotors produced at several plants of

the Russian military industry. The coatings obtained, as compared to polymer coatings, exhibit higher hardness, comparable to that of nickel coatings, and, as compared to nickel coatings, exhibit higher uniformity, comparable to that of polymer coatings prepared by electrodeposition. Furthermore, high corrosion-protecting properties of nickel–polymer coatings make it unnecessary to include the phosphatization step into the painting technology.

## CONCLUSIONS

(1) Preparation of nickel–polymer coatings by joint cathodic electrodeposition from a solution of polymeric electrolytes and nickel acetate was studied. The nickel–polymer coatings obtained exhibit the layer-by-layer composition heterogeneity. The lower layer is a composite containing iron–nickel intermetallic compound (“meteorite iron”).

(2) The nickel–polymer coatings have 3 times higher degree of cross-linking compared to the nickel-free coatings, which may be due to the catalytic action of nickel on the curing process. Preservation of high elasticity suggests possible formation of fractal clusters of nanosized nickel particles in the coating. There are good conditions for formation of such clusters in the near-electrode layer in the presence of the polymer.

(3) A paint-and-varnish formulation for preparing wear-resistant corrosion-protecting coatings combining enhanced hardness and high elasticity was developed on the basis of the nickel–polymer film-forming agent.

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