

## IMPROVEMENT OF THE OPERATIONAL AND MAINTENANCE PERFORMANCE CHARACTERISTICS OF WATER TRANSPORT EQUIPMENT SURFACES THROUGH THE IMPLEMENTATION OF POLYMER COATINGS

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*The paper presents the results of experimental studies aimed at improving the operational and repair characteristics of water transport surfaces by developing and implementing new polymer coatings with improved anti-corrosion characteristics. The main purpose of the study is to establish the patterns of the influence of heterogeneously dispersed fillers on the corrosion resistance of epoxy composite coatings. The epoxy oligomer ED-20, polymerized with polyethylenepolyamine (PEPA), was used as a matrix for protective coatings. To modify the polymer structure, a filler system was used, which includes a nanodispersed fullerene-carbon black mixture (30–40 nm) and microdispersed trimethoprim (5–10 μm). Optimization of the composition was carried out using the method of mathematical planning of experiments in the STATGRAPHICS® Centurion XVI software environment. Corrosion resistance was studied using impedance spectroscopy, which determined the electrical resistivity and capacitance of the coatings in three model aggressive media: a 10% sulfuric acid solution, acetone, and seawater (35%). It was found that the introduction of trimethoprim contributes to additional chemical crosslinking of the polymer matrix, while the nanodispersed filler forms the effect of a “labyrinth structure”, reducing the diffusion permeability of the coating. It was experimentally confirmed that the developed compositions increase resistivity (0.25–0.29 Ω·m<sup>2</sup>) and decrease capacitance (16–27 pF/m<sup>2</sup>), indicating the formation of a dense, hydrophobic, and structurally stable polymer network. The maximum values of the studied parameters are characterized by the EC-3 coating, which exceeds the performance of the base matrix by 56% and HEMPEL, HEMPALIN ENAMEL coatings by 24–28%. A generalized model of the mechanism underlying increased corrosion resistance is proposed, based on three key processes: chemical crosslinking, nanomodification, and hydrophobicization of the polymer structure.*

**Key words:** water transport; navigation equipment; anti-corrosion protection; coating composition; model; marine environment.

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**Problem statement.** The problem of protecting water transport surfaces against corrosion stems from the fact that a significant number of components, mechanisms, and equipment are made of steel and iron-based alloys and are installed in open areas (decks), which involve operation in conditions of intense exposure to an external aggressive environment. Even materials with increased corrosion resistance are subject to deterioration under the influence of seawater, atmospheric moisture, salt fog, acid rain, and organic solvents. This, in turn, leads to deterioration in the operational characteristics of structures and a decrease in their reliability and durability. This

problem is quite relevant for deck mechanisms and metal structures, including navigation equipment, which are constantly exposed to variable climatic and mechanical loads. The destruction of protective coatings and the appearance of microcracks and defects contribute to the penetration of corrosive components into the metal base, which initiates electrochemical corrosion processes. The consequence of this is not only the deterioration of the equipment's technical condition, but also significant economic costs associated with the repair and maintenance of these elements [1–3]. Therefore, the task of developing new protective coatings for shipboard equipment is directly related to the problems of technical operation, maintenance, and repair of water transport facilities, which determines the practical relevance of the study to the thematic scope of the journal in the field of transport technologies and transport service systems.

**Analysis of recent publications and research.** In most scientific works, considerable attention is paid to increasing the corrosion resistance of polymer coatings by introducing nanodispersed fillers. In particular, in [4, 5], it was established that nanoparticles of metal oxides and carbon materials contribute to the formation of a “labyrinthine structure”, which significantly complicates the diffusion of water, oxygen, and ions to the metal surface. Similar results are reported in [6], which demonstrate the effectiveness of using carbon nanostructures to enhance the barrier properties of epoxy systems. At the same time, an important direction is the chemical modification of the polymer matrix. In the works [7, 8], it was shown that the introduction of amine-containing organic compounds increases the crosslinking density of the polymer network, thereby improving the mechanical and anti-corrosion characteristics of coatings. However, such approaches are mostly considered separately from the use of nanofillers. In works [9–11], it is shown that the combination of differently dispersed fillers allows simultaneous increases in the density of the polymer structure, reductions in permeability, and improvements in the mechanical stability of coatings during operation. At the same time, the analysis of literary sources indicates that the use of active organic compounds as structural modifiers of epoxy coatings remains insufficiently studied. In particular, there are no systematic studies devoted to assessing their influence on the crosslinking of the polymer matrix, the formation of the microstructure, and the long-term corrosion resistance in aggressive environments.

**The purpose of the work** is to investigate the effect of differently dispersed fillers on the corrosion resistance of protective coatings.

**Materials and research methods.** To create new protective coatings, an epoxy oligomer of the ED-20 brand (ISO 18280:2010) was used, and the polymerization was performed with an amine-type hardener, polyethylenepolyamine PEPA (TU 6-02-594-73).

To improve the corrosion resistance of the developed coatings, the following were used: nanodispersed fullerene-carbon black mixture (NFCM), 30...40 nm; biocidal filler trimethoprim  $C_{14}H_{18}N_4O_3$  (TMP), 5...10  $\mu m$ . Optimization of the content of heterogeneously dispersed fillers in the epoxy binder when creating new protective coatings was performed using the STATGRAPHICS® Centurion XVI software package.

The modified epoxy matrix was prepared according to the procedures described in the works [12–15].

The corrosion resistance of the developed and known protective coatings was determined by measuring changes in specific resistance and specific capacitance using an RLC meter (type E7-22). The thickness of the coatings was measured using a CM8811FN thickness gauge. The study was carried out for 30 days at  $T = 293 \pm 2$  K. The obtained values of the specific resistance and specific capacitance of the coatings were converted using the formulas:

$$\rho = \rho \cdot S, \Omega \cdot m^2 \quad (1)$$

$$c = C/S \text{ pF}/m^2 \quad (2)$$

$$S = \pi D^2/4, m^2 \quad (3)$$

The base material was selected as shipbuilding structural steel Q235, measuring 80×40×2.0 mm, used for the manufacture of hull and internal structures of ships where high loads are not expected, in particular, elements of navigation equipment. At the same time, the working area of the coatings was 0.00512 m<sup>2</sup> (the area on both sides of the plate was taken into account, taking into account the side surface with a thickness of 2.0 mm).

**Research results and their discussion.** The operation of ship equipment and mechanisms occurs under conditions of intensive exposure to aggressive environments, which increases the requirements for the protective characteristics of coatings. In this regard, increasing the corrosion resistance of polymer coatings used to protect metal structures is particularly important. The effectiveness of such materials is determined not only by their initial properties, but also by the ability to maintain operational characteristics over a long period of operation in difficult marine environment conditions. At the same time, one of the determining indicators of the functional suitability of polymer coatings is their barrier ability, i.e., the ability to limit or significantly slow down the diffusion of corrosive components, such as water, oxygen, and salt ions, to the surface of the metal base. The penetration of these agents initiates electrochemical processes that lead to material degradation and corrosion of metal surfaces, even those made of alloys. An equally important characteristic is the ability of coatings to maintain a high level of adhesion to the substrate, ensuring reliable contact between the polymer layer and the metal, as well as sufficient cohesive strength, which determines the integrity of the coating. Loss of adhesive or cohesive strength leads to the formation of defects, microcracks, and delaminations, which significantly accelerate the penetration of aggressive media and, accordingly, the corrosion destruction of metal surfaces. In addition, the operational durability of polymer systems largely depends on their resistance to external factors, in particular, high humidity, temperature fluctuations, ultraviolet radiation, and the influence of chemically active substances. Prolonged exposure to external factors leads to the physicochemical degradation of the polymer matrix, accompanied by structural transformations and a decrease in the coatings' barrier and protective properties. For water transport, these effects are especially critical for navigation equipment housings, foundation pedestals, deck-mounted support elements, exposed metal casings, and other functional surfaces that require stable performance characteristics during long-term service. In this regard, the developed coatings should be considered not only as new material compositions, but also as a practical means of increasing the operational reliability and maintainability of ship equipment, which corresponds to the thematic area J5. In this regard, optimizing the structure and physical-mechanical and diffusion characteristics of coatings to minimize their permeability to corrosive agents is one of the priority areas of research in the field of knowledge "Transport and Services". The results obtained can be used to improve the corrosion and wear resistance of vehicle surfaces, thereby increasing operational reliability and reducing maintenance and repair costs.

The study used a basic epoxy matrix and developed a series of protective coatings based on ED-20 epoxy resin using a bidisperse filler: dispersed trimethoprim (5...10 μm), nanodispersed fullerene-carbon black mixture (30...40 nm). It should be noted that the optimization of the heterogeneous filler content in the epoxy binder was performed using the STATGRAPHICS® Centurion XVI application package. Based on the obtained mathematical models [14], the following compositions of protective coatings were obtained, which were tested in various aggressive environments:

- EC 1 – control matrix (epoxy resin ED-20 + hardener PEPA);
- EC 2 – epoxy resin ED-20 (100 %) + hardener PEPA (10.0 %) + trimethoprim (5.0 %) + nanodispersed fullerene-carbon black mixture (0.050 %);
- EC 3 – epoxy resin ED-20 (100 %) + hardener PEPA (10.0 %) + trimethoprim (10.0 %) + nanodispersed fullerene-carbon black mixture (0.050 %);
- EC 4 – epoxy resin ED-20 (100 %) + hardener PEPA (10.0 %) + trimethoprim (15.0 %) + nanodispersed fullerene-carbon black mixture (0.050 %).

The values of the specific resistance and specific capacitance of the developed protective epoxy composite coatings were compared with the values of 2 known coatings HEMPEL (white

color) and HEMPALIN ENAMEL (yellow color), which are used to protect elements of navigation equipment (Fig. 1).

HEMPEL coating (white color) is intended for anti-corrosion protection of metal structures, in particular decks, superstructures and elements of navigation equipment of ships.

HEMPALIN ENAMEL (yellow color) is intended for visual identification of dangerous objects, in particular elements of navigation equipment.

Thus, the selected comparison objects and the illustrated application areas confirm the direct practical orientation of the study toward shipboard technical systems and navigation equipment, rather than toward generalized laboratory models only. This strengthens the applied significance of the work for the field of water transport operation and maintenance.



Figure 1 – Navigation equipment of the container ship SPYROS V with applied coatings (arrows show: coating of elements of foundation pedestals for fastening elements of navigation equipment; surfaces for visual identification of dangerous objects that are a source of electromagnetic radiation)

The corrosion resistance was determined using impedance spectroscopy at 1 kHz over 30 days of immersion of samples in model aggressive environments: 10% sulfuric acid solution ( $\text{H}_2\text{SO}_4$ ), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), and seawater (35‰,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ). The choice of these environments is due to the following:

1. Sulfuric acid solution ( $\text{H}_2\text{SO}_4$ ) is a typical component of acid rain, which can settle on the hull of a ship or navigation equipment during a prolonged stay in ports with a high level of industrial pollution.

2. Acetone ( $\text{C}_3\text{H}_6\text{O}$ ) is a polar organic solvent that well simulates the process of swelling, dissolution of weakly cross-linked areas of the polymer, and therefore allows you to assess the resistance of the coating to dissolution and leaching.

3. Seawater is a permanent working environment that comes into contact with ship equipment, in particular navigational instruments installed on the deck or on open superstructures. Accordingly, direct contact with seawater spray and atmospheric moisture is formed. Salinity of 35‰, which is equivalent to 35 g/kg NaCl, corresponds to the conditions of the open ocean and provides an adequate simulation of sea voyages.

The experimental testing methodology involved tracking the dynamics of changes in the specific resistance of coatings ( $\rho$ ,  $\Omega \cdot \text{m}^2$ ) and specific capacitance ( $c$ ,  $\text{pF}/\text{m}^2$ ), which are integral characteristics of the anti-corrosion barrier.

Before applying both developed and commercial protective coatings manufactured by Hempel, a comprehensive preparation of the metal substrate was carried out. The preparatory operations included mechanical surface treatment to remove oxide films, corrosion products, and surface contaminants (Fig. 2). In addition, such treatment contributed to the formation of a developed microrelief structure of the surface, which provides an increase in the contact area and, accordingly, improved adhesive interaction of the coating with the substrate. Additionally, the

surface was degreased with acetone ( $C_3H_6O$ ), an organic solvent that effectively removes both polar and non-polar organic contaminants, thereby improving wetting of the metal surface by the developed polymer composition. Coatings were applied to samples on both sides, made of shipbuilding structural steel grade Q235 with dimensions of  $80 \times 40 \times 2.0$  mm. This approach provided a unified framework for evaluating the effectiveness of both developed and known coatings in experimental research.



Figure 2 – Experimental specimens made of shipbuilding structural steel Q235

After preparatory operations on the metal substrate, protective coatings of various compositions were applied using pneumatic spraying (Fig. 3). The use of this method makes it possible to assess the technological properties of the compositions from the standpoint of their practical suitability for use in the field of maritime transport, in particular during maintenance of equipment for navigation systems of ships. Pneumatic spraying ensures the formation of a uniform, thin-layer, homogeneous coating by dispersing the material over the surface, meeting the conditions for mechanized or automated application in dock and operational (ship) conditions. A similar approach allows us to assess the ability of epoxy compositions to self-level and their tendency to form a continuous, defect-free film. These characteristics are critically important for protecting navigation equipment, which is subject to increased requirements for corrosion resistance and operational reliability. Thus, the applied approach ensures obtaining objective information on the behavior of coatings in conditions as close as possible to the real operation of sea vessels and the performance of routine maintenance work.

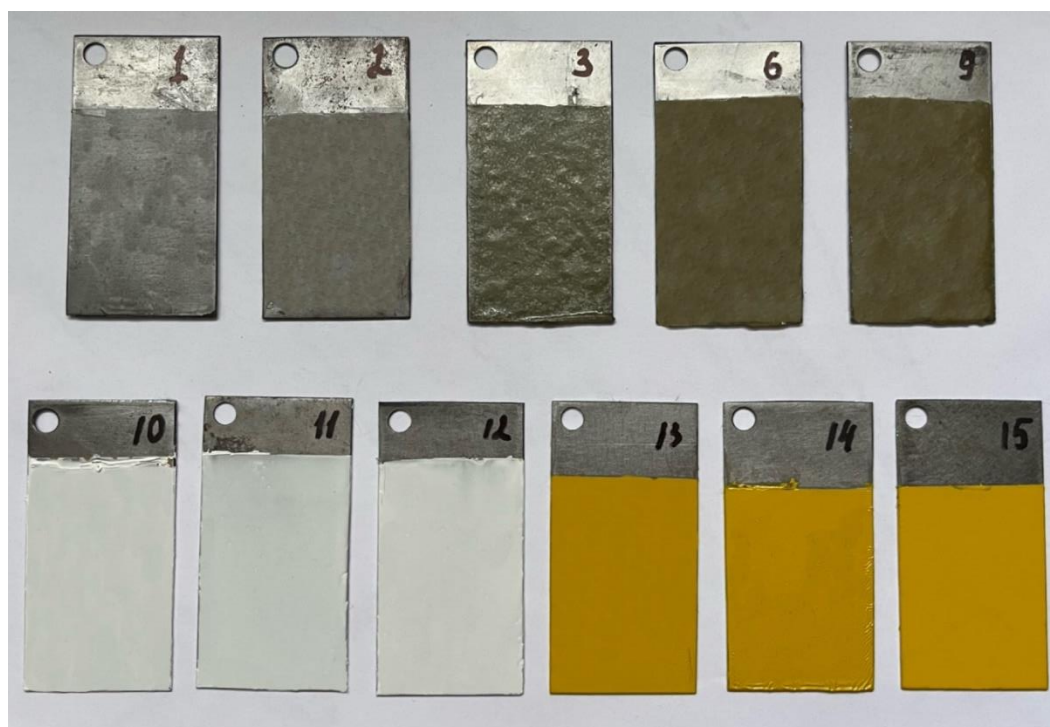


Figure 3 – Appearance of coatings applied by pneumatic method: 1, 2 – EC-1; 3 – EC-2; 6 – EC-3; 9 – EC-4; 10, 11, 12 – HEMPEL; 13, 14, 15 – HEMPALIN ENAMEL

*Study of the values of resistivity and specific capacitance in a sulfuric acid environment* (Table 1, 2). According to the results of the analysis of experimental studies obtained during 30-day exposure, it was found that the control coating EC-1 is characterized by the lowest values of resistivity, which monotonically decreases from  $\rho = 0.19\text{--}0.21 \Omega \cdot \text{m}^2$  (during the first 10 days) to  $\rho = 0.16 \Omega \cdot \text{m}^2$  (after 20 days of exposure in an aggressive environment). Such dynamics is due to the increased permeability of the epoxy matrix for hydrogen ions ( $\text{H}^+$ ) and sulfate ions ( $\text{SO}_4^{2-}$ ), which intensify the processes of physicochemical destruction of the polymer network. At the same time, an increase in the specific capacitance of the experimental samples from  $c = 21 \text{ pF/m}^2$  to  $c = 35 \text{ pF/m}^2$  was observed, which indicates a gradual saturation of the polymer volume with ionized particles, probably due to the existing structural defects.

Table 1 – Resistivity values obtained during the study of protective coatings

Name of coatings	$\rho$ (Sulfuric acid), $\Omega \cdot \text{m}^2$				$\rho$ (Acetone), $\Omega \cdot \text{m}^2$				$\rho$ (Seawater), $\Omega \cdot \text{m}^2$			
	Trial period, days											
	0	10	20	30	0	10	20	30	0	10	20	30
EC-1	0.21	0.19	0.16	0.16	0.23	0.21	0.18	0.18	0.24	0.22	0.22	0.22
EC-2	0.28	0.27	0.23	0.23	0.30	0.29	0.25	0.25	0.30	0.29	0.28	0.28
EC-3	0.28	0.27	0.27	0.25	0.30	0.29	0.26	0.26	0.30	0.29	0.29	0.29
EC-4	0.27	0.24	0.22	0.22	0.29	0.26	0.25	0.25	0.30	0.28	0.28	0.28
HEMPEL	0.27	0.24	0.19	0.19	0.29	0.25	0.21	0.21	0.29	0.28	0.23	0.23
HEMPALIN ENAMEL	0.27	0.23	0.19	0.18	0.29	0.21	0.17	0.17	0.29	0.28	0.24	0.24

Table 2 – Specific capacitance values obtained during the study of protective coatings

Name of coatings	$c$ (Sulfuric acid), $\text{pF/m}^2$				$c$ (Acetone), $\text{pF/m}^2$				$c$ (Seawater), $\text{pF/m}^2$			
	Trial period, days											
	0	10	20	30	0	10	20	30	0	10	20	30
EC-1	24	30	35	35	24	35	39	40	24	27	28	28
EC-2	16	20	21	21	16	25	30	28	16	17	19	19
EC-3	15	20	22	22	15	29	29	27	15	16	16	16
EC-4	17	23	24	24	17	29	30	29	17	17	18	18
HEMPEL	22	29	33	33	20	27	31	31	23	27	27	27
HEMPALIN ENAMEL	24	29	36	36	25	35	42	42	24	27	30	30

The results obtained indicate insufficient barrier efficiency of the coating, which is associated with the presence of microdefects and the diffusion-open morphology of the polymer matrix. The combination of these defects accelerates the penetration of an aggressive environment to the metal base. At the same time, the developed epoxy composite coatings – EC-2, EC-3, EC-4 demonstrate improved protective characteristics, in particular, reduced permeability of aggressive components. The values of the specific resistance for samples EC-2 and EC-4 exceed the similar indicator of the control coating by 37–43% (Table 1). The highest resistivity value among the developed coating compositions was found for EC-3 ( $\rho = 0.27 \Omega \cdot \text{m}^2$ ). The increase in resistivity by 56% compared to the control sample indicates the formation of a denser and structurally ordered coating, which complicates the diffusion of aggressive ions in its volume.

The study's results suggest that trimethoprim, owing to its pronounced amine functional groups, can interact with the epoxy matrix by forming chemical bonds with epoxy groups. This

process contributes to additional crosslinking of polymer chains, leading to a denser, structurally stable polymer network. As a result, the cohesive strength of the coating increases, its permeability to aggressive ions and water molecules decreases, and its resistance to physicochemical degradation in corrosive environments increases. In addition, enhanced crosslinking of the polymer can reduce the formation of micropores and microcapillaries within the polymer volume, further improving the material's barrier properties. The introduction of a nanodispersed fullerene-carbon black mixture performs several equally important functions. Firstly, nanoparticles fill the existing nanopores and other defects of the polymer matrix, creating an additional physical barrier for the diffusion of ionized and molecular components of the aggressive environment. Secondly, nanosized particles can distribute mechanical stresses in the coating during operation, thereby reducing the formation of cracks and defects in the polymer layer. Thirdly, the fullerene-carbon black phase can partially interact with the polymer matrix, increasing its structural integrity and stability over a long period of exposure and, therefore, during operation. Thus, the combination of trimethoprim and nanodispersed filler produces a synergistic effect, enhancing the barrier and durability of epoxy coatings.

Experimental data obtained for known HEMPEL and HEMPALIN ENAMEL coatings show that, under sulfuric acid conditions, on the 30th day of testing, the resistivity of the samples exceeds that of the similar indicator for the unfilled epoxy coating by 12–18%. This indicates a slight increase in barrier ability, due to partial compaction of the polymer and limited physicochemical interactions among the components in these coatings' compositions. At the same time, the resistivity indicators remain 24–28% lower than those of the developed EC-3 coating, indicating a significantly higher efficiency of the developed coating compositions in preventing the penetration of aggressive ions and molecules into the metal base.

Such a comparison emphasizes the importance of chemical modification of the polymer matrix and the introduction of nanodispersed compounds to increase the operational reliability of the coatings. In practical terms, the 56% increase in resistivity relative to the control sample (unmodified epoxy matrix) indicates the formation of a denser, structurally ordered polymer network, which significantly hinders the diffusion of corrosive ions within the developed coating. This is critical for protecting metal surfaces from degradation in highly corrosive environments, such as seawater and acidic solutions, which are common during long-term operation of water transport surfaces. From the standpoint of practical application, this result means that the developed EC-3 coating can provide longer preservation of the functional state of ship equipment surfaces, slower development of under-film corrosion, a lower probability of coating failure during service, and reduced frequency of scheduled repair interventions. In addition, improved barrier characteristics create prerequisites for extending maintenance intervals and lowering operating costs for shipboard structures and navigation equipment exposed to aggressive marine factors.

*Study of the values of resistivity and specific capacitance in an acetone environment.* A comprehensive analysis of experimental data indicates that acetone, as an organic solvent, affects the polymer coating through several interrelated mechanisms. First, the solvent causes swelling of the material due to the penetration of acetone molecules into the free volumes of the polymer's amorphous phase. Second, acetone partially dissolves weakly cross-linked matrix fragments, leading to local disruption of polymer chain cohesion and the formation of microdefects in the coating structure. In the control sample EC-1, these processes are shown as a gradual decrease in resistivity from  $\rho = 0.23 \Omega \cdot \text{m}^2$  (at the beginning of exposure) to  $\rho = 0.18 \Omega \cdot \text{m}^2$  (after 30 days of exposure in an aggressive environment). At the same time, an increase in the specific capacitance from  $c = 24 \text{ pF/m}^2$  to  $c = 40 \text{ pF/m}^2$  was observed. The increase in capacitance indicates the accumulation of polar solvent molecules within the polymer volume, leading to increased dielectric polarization and destruction of the matrix's amorphous phase. These changes indicate a high permeability of the control coating for polar molecules and its limited barrier ability during a long exposure period. Significantly more stable studied parameters characterize the developed epoxy compositions EC-2, EC-3, and EC-4. After 30 days of exposure, the resistivity of these samples remained within the range of  $\rho = 0.25\text{--}0.26 \Omega \cdot \text{m}^2$ , and the specific capacitance did not exceed

$c = 27\text{--}29$  pF/m<sup>2</sup>. Such stability is explained by the formation of a three-dimensional, densely crosslinked, hydrophobic polymer network that significantly limits acetone penetration. In addition, the presence of trimethoprim in the coating as a structural modifier enhances synergistic effects: trimethoprim promotes additional chemical crosslinking of polymer chains, while nanoparticles fill nanopores and defects, increasing the barrier properties and mechanical stability of the coating.

Comparative analysis showed that the resistivity of commercial HEMPEL coatings after 30 days of exposure in an acetone environment exceeds the indicator of the unmodified epoxy matrix by 16%, but remains 19% lower than that of the developed EC-3 coating. The alkyd coating HEMPALIN ENAMEL demonstrates a decrease in resistivity by 5.5% compared to the epoxy matrix. This difference is explained by the chemical nature of the polymer systems: alkyd coatings are polyesters modified with fatty acids or oils, with a lower crosslinking density and a more polar structure containing hydrophilic groups (–OH, –COOH). These groups actively interact with polar solvents, increasing permeability and leading to a more pronounced decrease in the coating's barrier properties. Thus, the results obtained demonstrate the complex effect of the solvent on the studied characteristics of polymer coatings. Penetration of acetone molecules into the free volume and micropores leads to swelling and partial destruction of the amorphous phase, a decrease in resistivity, and an increase in specific capacitance. At the same time, the introduction of trimethoprim (as a modifying additive) and nanofiller into the polymer matrix enabled the creation of a denser, hydrophobic, and three-dimensionally crosslinked network, which reduces the diffusion of polar molecules, maintains the stability of electrophysical parameters, and increases the operational reliability of coatings in aggressive environments. These data are important for optimizing the composition of epoxy coatings and ensuring their high resistance to organic solvents in marine and industrial practice.

*Study of resistivity and capacitance values in seawater* (Table 1, 2). In seawater, the epoxy matrix EC-1 was characterized by a resistivity  $\rho = 0.22\text{--}0.24$  Ohm·m<sup>2</sup>, a decrease in which was observed after the tenth day of exposure. A similar effect indicates partial hydration and diffusion of chloride ions to the metal substrate. At the same time, the specific capacitance was  $c = 24\text{--}28$  pF/m<sup>2</sup>, indicating the partial presence of water molecules in the polymer's pores. Regarding the studied epoxy composite coatings, we can state that they exhibit high barrier characteristics, as the values of the studied resistivity and capacitance did not change significantly over the entire exposure period (30 days). The obtained values of resistivity and capacitance indicate the formation of a dense structural-hydrophobic network that effectively prevents the penetration of moisture and aggressive chloride ions into the metal base.

As in previous model aggressive environments, the obtained values of resistivity and capacitance of known coatings from HEMPEL and HEMPALIN ENAMEL are greater than the value of the resistivity of the epoxy matrix, but are less than the value of the resistivity of the EC-3 coating.

Analysis of the obtained parameters allows us to state the following. The control epoxy coating EC-1 is characterized by a resistivity within  $\rho = 0.22\text{--}0.24$  Ω·m<sup>2</sup> at the initial stage of exposure. After the tenth day of exposure, a gradual decrease in the studied indicator was observed. The decrease in resistivity can be explained by the partial hydration of the amorphous phase of the polymer matrix and by the diffusion of chlorine ions (Cl<sup>-</sup>) toward the metal substrate. Water molecules penetrating the matrix pores increase the specific capacitance from  $c = 24$  pF/m<sup>2</sup> to  $c = 28$  pF/m<sup>2</sup>, indicating the initial integration of the polar environment into the polymer's internal volume and a partial change in the coating's dielectric properties. These processes are a typical manifestation of the electrochemical interaction of the polymer matrix with aggressive components of seawater, which can lead to a local decrease in the material's barrier efficiency and the development of the initial stages of corrosion on the metal base. The developed coatings (EC-2, EC-3, EC-4) exhibit much more stable properties. During 30 days of exposure, the specific resistance remained practically unchanged at  $\rho = 0.25\text{--}0.26$  Ω·m<sup>2</sup>, and the specific capacitance did not exceed  $c = 27\text{--}29$  pF/m<sup>2</sup>. Such stability indicates the formation of a dense, three-dimensionally crosslinked, hydrophobic polymer network that effectively limits the penetration of ions and water molecules.

Modification of the polymer structure with trimethoprim enhances crosslinking, increasing the cohesive strength and structural integrity of the matrix. The nanodispersed fullerene-carbon black mixture fills the existing nanopores and defects, thereby reducing capillary permeability and increasing the material's barrier properties.

A comparative analysis of the studied parameters of known coatings manufactured by HEMPEL and HEMPALIN ENAMEL showed that the resistivity of these systems exceeds the corresponding indicators of the unmodified epoxy matrix, but remains lower than that of the EC-3 coating. This emphasizes the advantages of the developed compositions, since their three-dimensional structure provides the maximum barrier for the diffusion of chlorine ions and water molecules. The HEMPALIN ENAMEL alkyd coating, unlike epoxy systems, demonstrates a decrease in resistivity by 5.5% compared to the epoxy matrix, which is explained by the chemical nature of alkyd polymers: they are polyesters modified with fatty acids or oils, with a lower crosslinking density and the presence of polar hydrophilic groups ( $-\text{OH}$ ,  $-\text{COOH}$ ), which actively interact with polar components of seawater. Thus, the results obtained demonstrate the complex influence of the marine environment on the characteristics of the developed and known polymer coatings. Unmodified epoxy systems exhibit a gradual decrease in barrier properties due to hydration and ion diffusion, whereas modified coatings with a three-dimensionally crosslinked, hydrophobic structure maintain stable resistivity and capacitance throughout the entire exposure period. This emphasizes the feasibility of using modified epoxy compositions to protect metal structures in the marine and coastal industries, as they provide high resistance to the penetration of aggressive components of seawater, reduce the risk of corrosion, and extend the service life of structures and functional surfaces in water transport. The obtained effect is of direct practical importance for the maintenance of navigation aids, deck equipment, open-area metal assemblies, and fastening elements of marine technical systems, where corrosion damage usually leads to deterioration in reliability, increased maintenance labour intensity, and additional repair costs.

At the same time, the obtained results allow explaining the mechanism of increased corrosion resistance in seawater, based on the presented model (Fig. 4), which includes: chemical crosslinking, nanomodification, and hydrophobization of the structure.

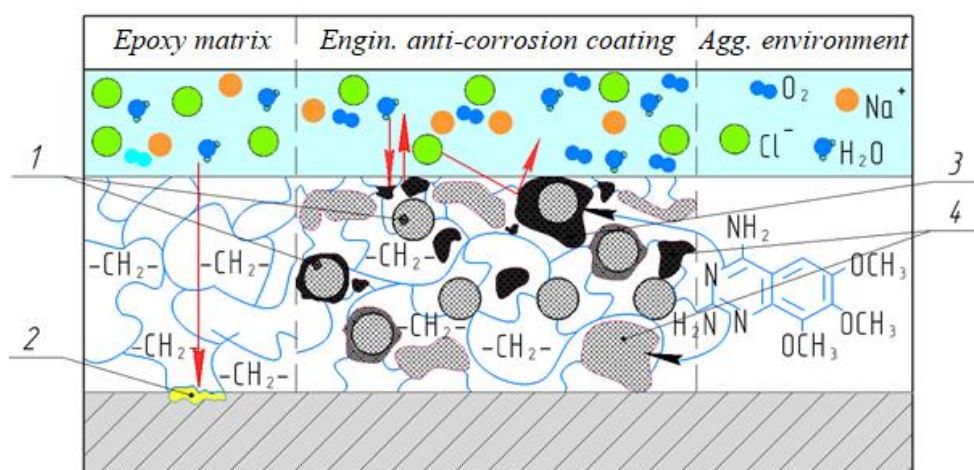


Figure 4 – Model of the mechanism for increasing the corrosion resistance of the developed epoxy composite protective coatings in the seawater environment: 1 – schematic representation of nanoparticles; 2 – nucleation of sub-film corrosion; 3 – adsorption of  $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$  on the surface of particles of the nanodispersed fullerene-carbon black mixture; 4 – formation of new structures  $\text{CH}(\text{OH})-\text{CH}_2-\text{NH}-\text{R}_2$  ( $\beta$ -hydroxamine) in the polymer bulk

If we consider the mechanism of chemical crosslinking, then trimethoprim performs the function of additional hardening due to the presence of two primary amino groups interacting with the epoxy rings of the epoxy oligomer ED-20 (proven by the method of wide-angle X-ray diffraction and IR spectral analysis) [13]. This forms additional covalent bonds, increasing the network density and reducing the diffusion permeability of the epoxy composite coating to the base. While the epoxy matrix does not contain, in its structure, characteristic barriers that reduce the

diffusion permeability to the metal base, which accordingly affects the values of the specific resistance and specific capacitance.

If we consider the mechanism of nanomodification, the introduction of nanodispersed fullerene-carbon black mixture 1 forms a diffusion barrier due to the "labyrinth structure", increasing the time required and complicating the path of water molecules and dissolved ions through the polymer matrix to the base.

Hydrophobization of the structure. First of all, it is necessary to take into account that new structures 4 ( $\beta$ -hydroxyamine structures  $\text{CH}(\text{OH})\text{-CH}_2\text{-NH-R}_2$ ) form in the volume of the modified polymer, which, in terms of strength indicators, prevail over the basic ones [14]. It is also necessary to consider the adsorption of  $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3$  on the surface of particles of the nanodispersed fullerene-carbon black mixture due to the  $\pi$ - $\pi$  interaction 3. However, it is necessary to consider the complex effect of trimethoprim and the nanodispersed fullerene-carbon black mixture, which provides a decrease in the polarity of the coating due to a decrease in the number of free hydrophilic groups ( $\text{OH-}$ ,  $\text{-COOH}$ ), which is confirmed by lower capacitance values (relative to the control sample) for the developed epoxy composite coatings in all environments during 30 days of exposure. It is also possible to consider the stabilization of the diffusion process over time, due to the stabilization of the specific resistance and specific capacitance over 30 days, indicating the absence of structural destruction and degradation at the interface between the phases "polymer-filler-substrate".

Based on the conducted experimental studies and the presented mechanism of increasing the corrosion resistance of the developed coatings, it was established that the most effective anti-corrosion coating is EC-3, which contains epoxy oligomer ED-20 (100 %), trimethoprim (10.0 %), nanofullerene-carbon black mixture (0.050 %), and hardener PEPA (10 %). The complex use of fillers provides not only a high level of protection in conditions of aggressive environments, but also stability over a long period of operation.

**Conclusions.** Based on the comprehensive studies conducted, the following was established.

1. It was experimentally proven that in three aggressive environments – acidic (10%  $\text{H}_2\text{SO}_4$ ), acetone ( $\text{C}_3\text{H}_6\text{O}$ ), saline solution (35‰,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) – the developed coatings provide significantly higher values of specific resistance (within  $\rho = 0.25\text{--}0.29 \Omega \cdot \text{m}^2$ ) and lower values of specific capacitance (within  $c = 16\text{--}27 \text{ pF/m}^2$ ), compared to the epoxy matrix and well-known coatings from HEMPEL and HEMPALIN ENAMEL. This indicates the effective formation of a stable, nano-strengthened, and hydrophobic polymer structure. Significant barrier protection is created by the sample EC-3 (100 % of epoxy oligomer ED-20 + 10.0 % of trimethoprim + 0.050 % of fullerene-carbon black mixture ED-20 + 10.0 % of hardener PEPA), which provided maximum protective characteristics in all studied environments, demonstrating minimal changes in the values of specific resistance and specific capacitance during 30 days of exposure. In practical terms, the obtained results indicate the possibility of using the developed coating to improve the corrosion protection of navigation equipment, deck mechanisms, supporting metal structures, and other ship surfaces operated in aggressive marine conditions.

2. A model is proposed that reveals the idea of the mechanism of increasing the corrosion resistance of the developed epoxy composite coating modified with trimethoprim and a nanodispersed fullerene-carbon black mixture. The model is based on a comprehensive analysis of experimental results and summarizes the main structural and chemical processes that occur during the action of aggressive environments, in particular:

- chemical crosslinking of the polymer matrix due to the interaction of the primary amino groups of trimethoprim with the epoxy oligomer ED-20, which ensures the formation of additional covalent bonds and a decrease in the diffusion permeability of the coating;
- nanomodification associated with the formation of a labyrinth structure in the volume of the epoxy network due to the introduction of a nanodispersed fullerene-carbon black mixture, which inhibits the transfer of ions and molecules of the aggressive environment;
- hydrophobization of the polymer structure due to a decrease in the content of hydrophilic groups ( $\text{-OH}$ ,  $\text{-COOH}$ ), due to the synergistic action of fillers, including the  $\pi$ - $\pi$  interaction between trimethoprim and the graphite-like surface of the NFCM particles.

3. The practical effect of implementing the developed EC-3 coating consists in reducing the diffusion permeability of the polymer layer, slowing corrosion initiation on the metal substrate, preserving the protective integrity of the coating during prolonged exposure, and improving the operational and maintenance characteristics of water transport equipment surfaces. Compared with the base epoxy matrix, the developed composition demonstrated an increase in resistivity of up to 56%, and compared with commercial coatings HEMPEL and HEMPALIN ENAMEL, an advantage of 24–28%, which confirms its higher functional efficiency under simulated service conditions.

The developed epoxy composite coatings should be used to improve the operational and repair characteristics of metal structures and equipment for navigation aids used by vessels operating under prolonged exposure to aggressive environments.

**Prospects for further research.** Prospects for further research are associated with expanding the range of operational factors affecting the developed coatings, in particular by studying their resistance to ultraviolet radiation, cyclic temperature changes, mechanical wear, and long-term salt fog exposure. It is also advisable to investigate the adhesion strength of the coatings after prolonged service, their crack resistance, and the possibility of industrial implementation for the protection of shipboard navigation equipment, deck mechanisms, and other metal surfaces of water transport facilities.

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**Сапронов О. О., Сіманенков А. Л., Банга М. М., Даниленко Д. О., Шаранов В. Д., Сапронова А. В.**  
ПІДВИЩЕННЯ ЕКСПЛУАТАЦІЙНО-РЕМОНТНИХ ХАРАКТЕРИСТИК ПОВЕРХОНЬ  
ОБЛАДНАННЯ ВОДНОГО ТРАНСПОРТУ ШЛЯХОМ ВПРОВАДЖЕННЯ ПОЛІМЕРНИХ  
ПОКРИТТІВ

*У роботі наведено результати експериментальних досліджень, спрямованих на підвищення експлуатаційно-ремонтних характеристик поверхонь водного транспорту шляхом розроблення та впровадження новітніх полімерних покриттів із покращеними антикорозійними характеристиками. Основною метою дослідження є встановлення закономірностей впливу різнодисперсних наповнювачів на корозійну тривкість епоксидних композитних покриттів. Як матрицю для створення захисних покриттів використано епоксидний олігомер ЕД-20, який полімеризували поліетиленполіаміном (ПЕПА). Для модифікації структури полімеру застосовано систему наповнювачів, що включає нанодисперсну фулерено-сажову суміш (30–40 нм) та мікродисперсний триметоприм (5–10 мкм). Оптимізацію складу композиції здійснено із застосуванням методу математичного планування експерименту з використанням програмного середовища STATGRAPHICS® Centurion XVI. Дослідження корозійної стійкості виконано методом імпедансної спектроскопії шляхом визначення питомого електричного опору та питомої ємності покриттів у трьох модельних агресивних середовищах: 10 % розчині сірчаної кислоти, ацетоні та морській воді (35%). Встановлено, що введення триметоприму сприяє додатковому хімічному зшиванню полімерної матриці, тоді як нанодисперсний наповнювач формує ефект «лабіринтової структури», зменшуючи дифузійну проникність покриття. Експериментально підтверджено, що розроблені композиції забезпечують підвищення значення питомого опору (0,25–0,29 Ом·м<sup>2</sup>) та зниження питомої ємності (16–27 нФ/м<sup>2</sup>), що свідчить про формування щільної, гідрофобної та структурно стабільної полімерної сітки. Максимальними значеннями досліджуваних параметрів характеризується покриття ЕКП-3, яке перевищує показники базової матриці на 56 % та покриттів НЕМPEL, НЕМPALIN ENAMEL – на 24–28 %. Запропоновано узагальнену модель механізму підвищення корозійної стійкості, що базується на трьох ключових процесах: хімічному зшиванні, наномодифікації та гідрофобізації структури полімеру.*

**Ключові слова:** водний транспорт; навігаційне обладнання; антикорозійний захист; склад покриття; модель; морське середовище.

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