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Functional polymer nanocomposites with increased anti-corrosion properties and wear resistance for water transport

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Abstract: Corrosive Corrosive destruction and hydroabrasive wear is a serious problem in 12 the operation of machine parts and water transport mechanisms. It is promising to develop new 13 composite materials with improved properties to increase the reliability of transport vehicles. In this 14 regard, the use of new polymer-based materials, which are characterized by improved anti-corro-15 sion properties and wear resistance, is promising. In this work, therefore, for the formation of mul-16 tifunctional protective coatings, epoxy dian oligomer brand ED-20, hardener polyethylene polyam-17 ine PEPA, a mixture of nanodispersed compounds with a dispersion of 30...90 nm, fillers Agocel S-18 2000 and Waltrop with a dispersion of 8...12 microns, particles of iron slag with a dispersion of 60...63 19 microns are used for the formation of multifunctional protective coatings. Using the method of 20 mathematical planning of the experiment the content of additives of different physico-chemical na-21 ture in the epoxy binder is optimized to obtain fireproof coatings with improved operational char-22 acteristics. A mathematical model is developed for optimizing the content of components in the 23 formation of protective anti-corrosion and wear-resistant coatings for means of transport as a result 24 of the complex effect of a mixture of nanodispersed compounds, iron scale and Waltrop. 25

Based on the mathematical planning of the experiment, new regularities of increasing the 26 corrosion resistance and resource of means of transport are established due to the formation of 4 27 different protective coatings, which are tested for resistance to aggressive environments (technical 28 water – CAS N $^{\circ}$ 7732-18-5, gasoline – CAS N $^{\circ}$ 64742-82-1, acetone – CAS No. 67-64-1, I-20A lubricant 29 – CAS N $^{\circ}$ 64742-62-7, sodium solutions – CAS N $^{\circ}$ 1310-73-2, sulfuric acid – CAS N $^{\circ}$ 7664-93-9) and 30 hydroabrasive wear resistances. 31

A study of the change in the permeability index in aggressive environments is additionally 32 carried out, taking into account the rational ratio of dispersive fillers in the epoxy binder, which 33 made it possible to create an effective barrier to the penetration of aggressive water molecules to the 34 base. A decrease in the permeability of protective coatings by 2.0...3.3 times relative to the epoxy 35 matrix is achieved. 36

In addition, the wear resistance of the developed materials under the action of hydroabrasive 37 is investigated. The relative resistance of the CM to the action of hydroabrasive was found by the 38 method of materials and coatings testing on the gas-abrasive wear with a centrifugal accelerator. 39 This method enables one to model the real process of wear of mechanisms parts under the hydroabrasive action. It is shown that the coefficient of wear resistance of the developed materials is 1.3 times higher than that of the polymer matrix, which indicates the resistance of the composites to the influence of hydroabrasive environment. 43

As a result, modified epoxy composite protective coatings with improved anti-corrosion 44 properties and wear resistance under hydroabrasive conditions are developed. It is established that 45 the protective coating filled with particles of a mixture of nanodispersed compounds (30–90 nm), 46 iron scale ($60-63 \mu m$) and Waltrop ($8-12 \mu m$) has the lowest permeability indicators. The 47

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permeability in natural conditions of such a coating during the time t = 300 days of the study is $\chi = 48$ 0.5%, which is 3.6 times less than the similar indicators of the epoxy matrix.

It is substantiated that the protective coating filled with particles of a mixture of nanodispersed compounds (30–90 nm), iron scale (60–63 microns) and Agocel S-2000 (8–12 μ m) is characterized by the highest indicators of wear resistance. The coefficient of wear resistance under the action of hydroabrasive of such a coating is *K* = 1.75, which is 1.3 times higher than the similar indicators of the original epoxy matrix. 54

Keywords: epoxy resin; hardener; nanopowder; filler; corrosion; wear resistance; mechanical characteristics; water transport 56

1. Introduction

The development of transport technologies at the current stage creates conditions for 59 improving not only the logistics of international transportation, but also the development 60 of new materials with improved properties to increase the reliability of transport means 61 [1-8].

It should be noted that modern scientific and technical progress is impossible without 63 the creation of new special epoxy materials that have improved properties in the complex 64 [9-13]. In particular, these are stiffness and elasticity, hardness and superfluidity, solubility in water and gas permeability, heat resistance and dielectric properties, corrosion and 66 wear resistance. Such opposite properties, which exclude each other, are combined in 67 epoxy polymers. At the same time, today epoxy polymers are widely used in the operation 68 of water transport due to their unique consumer properties. 69

To improve the properties of polymers, including those based on epoxy plasticizers 70 and fillers are introduced into the oligomer [14-21]. It should be noted that the introduction of modifiers is promising, since such additives with a small content (1–5%) allow significantly increasing the indicators of adhesive and cohesive strength of epoxy composites 73 [10, 13, 20-29]. The latter, in turn, should be used in the form of matrices for protective 74 coatings of working parts, including during their repair in voyage conditions of sea and 75 river transport vessel. 76

Taking into account the above, researchers [15-18, 30-35] showed that with the devel-77opment of the transport industry, the efficiency of the restoration of parts and mechanisms78is important, while increasing their service life and maintainability is relevant. It is neces-79sary in this direction to use new materials that differ not only in improved properties, but80also in economic efficiency in their application [30, 31]. Anti-corrosion protection of parts81of river and sea transport is also important, which provides for an increase in the inter-82repair resource of their operation. In this regard, the use of nanofillers.83

In addition, today more and more attention is paid to the secondary processing of 84 metallurgical production waste, which allows, in addition to cleaning the environ-ment, 85 to save significant funds aimed at the disposal of the same waste [29, 36]. Therefore, it is 86 proposed to use waste of different composition as fillers for the formation of epoxy com-87 posites with increased operational characteristics in our work. The use of cheap fillers 88 (waste of industrial production), which, in addition to improving the operational charac-89 teristics of epoxy composites, contribute to reducing the cost of structural materials, is 90 beneficial from an economic point of view. It is interesting to use iron slag (IS) particles as 91 a filler, characterized by the following composition, %: SiO₂ – 0,803; Al₂O₃ – 0,36; Fe₂O₃ – 92 32,57; FeO – 64,85; MgO – 0,03; MnO – 0,44; CaO – 0,21; S – 0,031. Iron slag is a waste in 93 the production of steel at metallurgical enterprises. 94

The analysis of publications direction of researching the properties of epoxy CMs 95 indicates the need to introduce synthesized oxide or carbide fillers into the oligomer to 96 obtain materials with increased operational characteristics. It is proven [14-22] that the 97

introduction of dispersed particles into the resin, even in small quantities, ensures a 98 change in the speed of the course of physicochemical processes during the structure formation of CM. Moreover, not only the chemical and physical nature, but also the content 100 and dispersion of the particles are important in regulating the crosslinking processes of 101 epoxy CMs. 102

The development of coatings with synthesized microdisperse fillers can be interesting for industrial customers. This allows not only to improve the properties of coatings, but also to significantly reduce their costs. In addition, this approach simultaneously ensures the cost-effectiveness of the developed materials, and is beneficial from the point of view of ecology and environmental protection, which can be significant to the industry, and the development of any region as a whole.

Researchers [37, 38] formed ultrahard microdisperse powders by high-voltage electric discharge (VED) synthesis. The research results showed that as a result of the VED 110 treatment, all the treated particles were crushed and their phase composition changed 111 with the synthesis of high-modulus TiC and Fe₃C compounds. Similarly, the same authors 112 synthesized a mixture of powders from a charge of Al (15 %) + Ti (85 %) with the following 113 composition: Ti (75 %) + Al₃Ti (15 %) + Ti₃AlC₂ (10 %). 114

During our work, a nanodispersed filler is introduced into the binder to improve the properties of epoxy composites. The powder synthesized by us according to the technology described in the work [38] is used as a nanodispersed filler for experimental studies. 117 Nanopowder is a mixture of nanodispersed compounds (MNDC) and is characterized by 118 the following composition, $\%: Si_3N_4 - 90$, $I_2O_3 - 5$; $AI_2O_3 - 5$. Particle size is d = 30...90 nm. 119

With the use of these powders, the authors [37, 38] developed new epoxy composite 120 coatings to improve the operational characteristics of technological equipment. At the 121 same time, it should be noted that the problem of improving the anti-corrosion properties 122 and wear resistance of CM in the complex has not yet been finally resolved. The field of 123 polymer materials science, which covers the substantiation of the mechanism of interac-124 tion of composition ingredients during their structuring requires further fundamental re-125 search. It is precisely such processes during the formation of the structure of materials that 126 further determine their cohesive properties and, as a result, corrosion and wear resistance. 127

It should be noted that for this purpose, various methods of studying the properties 128 of materials are used in the work. On the one hand, there are methods for studying the 129 physical and mechanical properties of materials: modulus of elasticity when bending (ISO 178:2010) and impact resilience (ISO 179-1). On the other hand, a set of corrosion resistance 131 research methods are also used: 132

1. Corrosive resistance of the protective coatings is determined by immersion of spec-133imens in water and 10% sulfuric acid solution. The duration of exposition specimens with134a size of $60 \times 10 \times 10$ mm in aggressive media is 150 days at the temperature $T = 20 \pm 2^{\circ}$ C.135

2. The corrosion resistance of CM is also determined by immersing the samples in136technical water (CAS No. 7732-18-5), gasoline (CAS No. 64742-82-1), acetone (CAS No. 67-13764-1), I-20A lubricant (CAS No. 64742-62-7), solutions of sodium (CAS No. 1310-73-2), sul-138furic acid (CAS No. 7664-93-9). The duration of exposure of samples with a size of13960×10×10 mm in aggressive environments is 720 h at a temperature of $T = 293 \pm 2$ K.140

Wear resistance according to ISO 9352 is additionally investigated in the work. The relative resistance of the CM to the action of hydroabrasive was found by the method of materials and coatings testing on the gas-abrasive wear with a centrifugal accelerator. 143

In our opinion, only such a comprehensive approach to evaluating properties may 144 allow choosing a material that will be characterized by maximum durability during operation on water transport. 146

Taking this into account, the introduction of reactive microdisperse fillers, including147synthesized nano- and microdisperse powders, into the epoxy resin is relevant. Chemi-148cally active microdisperse fillers in the form of Agocel S-2000 (AC) (Mineral Building So-149lutions, Germany) and Waltrop (BT) (Waltrop, Germany) powders are used in the for-150mation of materials during our work. These are white and yellow powders, respectively,151

produced in Germany. They are used as fillers for functional purpose materials. The size 152 of the particles is $8...12 \mu m$. It is important to carry out research on determining the critical content of powders, which are waste products of industrial production, for the purpose of forming protective epoxy coatings for parts of technological equipment. In addition the combination of these fillers in the composite will be expedient and effective. This will allow obtaining a synergistic effect in improving their properties. 157

Based on the above, the authors assumed that the noted requirements are largely 158 satisfied when using a mixture of nanodisperse compounds, synthesized microdisperse 159 powders of Agocel S-2000 and Waltrop, and production waste in the form of iron slag 160 particles as filler. Such additives are sufficiently active to accelerate the processes of interphase structure formation relative to the original epoxy matrix. 162

The purpose of this study is to establish the regularities of the influence of the optimal 163 content of nano- and microdisperse filler based on a mixture of nanodispersed compounds, synthesized microdisperse powders of Agocel S-2000 and Waltrop, and production waste in the form of iron slag particles on the main mechanical, corrosion properties 166 and wear resistance of polymeric composites from the epoxy matrix. 167

At the same time, to achieve the goal, the authors plan to:

- as a result of the mathematical planning of the experiment, optimize the content of fillers to obtain epoxy composites with increased operational characteristics and protective coatings based on them, which work under the influence of hydroabrasives and aggressive environments;
- investigate the corrosion resistance of the developed materials in various aggressive environments;
- investigate the resistance to hydroabrasive action of the developed materials;
- issue recommendations on the creation of protective coatings based on the developed
 composites for their introduction into the industry.
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2. Materials and Methods

2.1. Materials

Epoxy dian oligomer brand ED-20 (ISO 18280:2010, Technobudresurs, Kyiv, Ukraine) 180 [14, 15. 181

Polyethylene polyamine (PEPA) hardener (TU 6-05-241-202-78, Technobudresurs, 182 Kyiv, Ukraine) [25].

The powder synthesized according to the technology described in the work [38] is 184 used as a nanodisperse filler for experimental studies. Nanopowder is a mixture of nanodispersed compounds (MNDC), %: $Si_3N_4 - 90$, $I_2O_3 - 5$; $AI_2O_3 - 5$ (table 1). Particle size is d = 30–90 nm. 187

Table 1. Characteristics of MNDC.

I_2O_3	Al ₂ O ₃
14	44
89	41
35	76
-	35

The optimal filler (MNDC) content is -q = 0.25-0.50 pts.wt. At the same time, the 190 destructive bending stresses increase from $\sigma_{fl} = 48.0$ MPa (for the unfilled matrix) to 191 $\sigma_{fl} = 58.0$ MPa, the modulus of elasticity at bending from E = 2.8 GPa (for the unfilled 192 matrix) to E = 4.0 GPa, impact resilience reduced from W = 7.4 kJ/m² (for unfilled matrix) 193 to W = 7.3 kJ/m².

Particles of Agocel S-2000 (AC) (Mineral Building Solutions, Germany) and Waltrop 195 (BT) (Waltrop, Germany) powders are used as microdisperse fillers for experimental 196

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Table 2. Characteristics of fillers.

is 8–12 µm.

Agocel S-2000	Waltrop
Round powder particles	Round powder particles
White	Yellow
Absent	Absent
140	220
660	520
5	12
5–7	6–8
1500	1950
1300	1650
	Agocel S-2000 Round powder particles White Absent 140 660 5 5 5–7 1500

studies (table. 2.). These are white and yellow powders, respectively, produced in Ger-

many. They are used as fillers for CM for construction purposes. The size of the particles

Additionally, iron slag particles (IS) are used as a filler, characterized by the follow-202 ing composition, %: FeO – 64,85; SiO₂ – 0,803; Al₂O₃ – 0,36; Fe₂O₃ – 32,57 at other. Iron slag 203 is a waste in the production of steel at metallurgical enterprises. Particle size is d = 60-204 63 µm. 205

2.2. Research methods

The elastic modulus was determined according to ISO 178:2010. Sample parameters 207are specified in the work [29]. The modulus of elasticity at axial deflection (longitudinal elasticity) is studied. Research is carried out according to the scheme of the 4th bend. The 209 test speed is 0.5...1.0 mm/min according to ISO 178:2010. 210

The impact resilience was determined according to ISO 179-1 on the MK-30 rebound 211 pendulum machine [10]. Sample parameters: $(63 \times 12 \times 12) \pm 0.5$ mm. 212

Corrosive resistance of the protective coatings is determined by immersion of speci-213 mens in water and 10% sulfuric acid solution. The duration of exposition specimens with 214 a size of 60 ×10 ×10 mm in aggressive media is 150 days at the temperature $T = 20 \pm 2^{\circ}C$. 215 Specimens with a mass 10.0–12.0 g prior to study and after exposition in aggressive media 216 are weighed on electronic scales DRS-8000 «Shimadzu» with an accuracy of 0.02 ± 0.001 g. 217

The calculation of the penetration of aggressive media was carried out according to 218 the following formula [28]. 219

The corrosion resistance of polymers was also determined by immersing samples in 220 technical water (CAS No. 7732-18-5), gasoline (CAS No. 64742-82-1), acetone (CAS No. 67-221 64-1), I-20A lubricant (CAS No. 64742-62-7), solutions of sodium (CAS No. 1310-73-2), sul-222 furic acid (CAS No. 7664-93-9). 223

The duration of exposure of samples with dimensions of 60×10×10 mm in aggressive 224 environments was 720 h at a temperature of $T = 293 \pm 2$ K. Samples with a mass of 1.0–1.2 225 g before research and after exposure in aggressive environments are weighed on analyti-226 cal balances of the VLR-200 brand with accuracy up to ±0.001 g. 227

Wear resistance of the sample was investigated according to ISO 9352. Sample pa-228 rameters: $(100 \times 100 \times 3) \pm 0.5$ mm. The sliding speed during wear was 0.28 m/s. When 229 evaluating the wear, the mass of the worn material was taken into account at the standard 230 length of the friction path. 231

The relative resistance of the polymers to the action of hydroabrasive was found by 232 the method of materials and coatings testing on the gas-abrasive wear with a centrifugal 233 accelerator. The method of conducting the experiment is given in detail in work [23]. The 234 relative intensity of wear is given by the following formula: 235

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$$I = \frac{m_0 - m_{end}}{m_0} \cdot 100\%,$$

where m₀ and m_{end}, kg, are the masses of the specimen at the beginning and at the end of the tests, respectively. 237

The coefficient of wear resistance is determined by the formula:

 $K = \frac{I_E}{I},$

where I_E – is the relative wear intensity of the standard (St 3 steel) %;	239
I – is the relative intensity of CM wear, %.	240
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The structure of the CM after friction was investigated on a XJL-17AT metallographic 242 microscope, which was equipped with a Levenhuk C310 NG (3.2 MegaPixels) camera. 243

The structure and microrelief of the surfaces are studied using the LEO EVO 50 scanning electron microscope (Zeiss, Germany).

While investigating the physical and mechanical properties of the epoxy material, the deviation of values within 5% of the nominal value was observed.

While investigating the corrosion resistance and hydroabrasive wear resistance of the 248 epoxy material, the deviation of values within 4-6% of the nominal value was observed. 249

Statistical Methods. The statistical processing of the obtained results was performed250using the software package for statistical data processing: Graph Pud Prism 8 (GraphPad251Software 2365 Northside Dr. Suite 560 San Diego, CA, 92108, USA), with the definition of252the Student's criterion.253

2.3. Materials forming technology

Epoxy composites were formed using the following technology: first, heating the 255 resin to a temperature of $T = 353 \pm 2$ K and then holding it at this temperature for a time 256 of $\tau = 20 \pm 0.1$ min; the hydrodynamic combination of oligomer and modifier over time τ 257 = 1 ± 0.1 min; ultrasonic treatment (UST) of the composition during the time $\tau = 1.5\pm0.1$ 258 min; cooling the composition to room temperature over time $\tau = 60 \pm 5$ min; introduction 259 of hardener and mixing of the composition over time $\tau = 5 \pm 0.1$ min. 260

The CM was hardened according to the regime [10, 14, 23].

3. Results and discussion

3.1. Mathematical Planning of the Experiment

During the operation of coatings intended for the protection of ship hulls, deck 264 mechanisms, and superstructures, the ability to maintain cohesive strength under the 265 influence of natural external factors is important. At the same time, the development of 266 the surface layer of the coating with high physical and mechanical properties (bending 267 modulus and impact resilience) allows counteracting the penetration of an aggressive 268 environment through the polymer to the base. Therefore, the optimal content of fillers: 269 Waltrop, Agocel S-2000, iron slag was determined in previous works. It was established 270 that the improvement of the properties of composite materials was observed when 271 Waltrop was introduced at a content of q = 10 pts.wt. At the same time, the destructive 272 bending stresses increase from σ_{fl} = 48.0 MPa (for the unfilled matrix) to σ_{fl} = 45.2 MPa, the 273 modulus of elasticity at bending from E = 2.8 GPa (for the unfilled matrix) to E = 4.0 GPa, 274 impact resilience from $W = 7.4 \text{ kJ/m}^2$ (for unfilled matrix) to $W = 7.9 \text{ kJ/m}^2$. The optimal 275 content of Agocel S-2000 filler is -q = 30 pts.wt. At the same time, the destructive stresses 276 during bending are $-\sigma_{fl}=38.2$ MPa, the modulus of elasticity during bending -277 E = 4.3 GPa, the impact resilience – W = 7.7 kJ/m². The optimal content of iron slag filler is 278 -q = 60 pts.wt. At the same time, the destructive stresses during bending are -279

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 σ_{fl} = 54.6 MPa, the modulus of elasticity during bending is *E* = 4.4 GPa, and the impact 280 resilience is *W* = 8.2 kJ/m². 281

However, the formation of composites with two-component filler is interesting from 282 a practical point of view, which, in our opinion, will allow improving the properties of the 283 studied CMs in the complex. In this context, it is expedient and necessary to use the 284 method of mathematical planning of the experiment, which will allow reducing the number of conducted studies and optimizing the content of ingredients to obtain CM with the 286 maximum indicators of the selected characteristics. 287

On the basis of the above, iron slag and Waltrop were used for mathematical planning of the experiment. Dispersion of particles according to granulometric analysis: iron scale $-60-63 \mu m$, Waltrop $-8-10 \mu m$. For standardization, as well as to simplify calculations, each component (filler) was coded with conventional units, taking into account the variation step (Table 3). 292

9 experiments (N = 9) were conducted, each of which was repeated three times (p = 293 3) to exclude systematic errors (Table 4). 294

Table 3. Levels of variables in conventional and natural scales .

Components	Factor	Medium level, Step of variation,		Values of variable levels (pts.wt.) corre- sponding to conventional units		
		<i>q</i> , pts.wt.	Δq , pis.wi.	-1	0	+1
The main filler – iron slag	<i>X</i> 1	70	10	60	70	80
Additional filler – Waltrop	<i>X</i> 2	20	10	10	20	30

Table 4. Experiment planning scheme.

Nº (u)	xo	X 1	X 2	$x_3 = x_1^2 - d$	$x_4 = x_2^2 - d$	$x_1 x_2$
1	1	-1	-1	0.33	0.33	+1
2	1	+1	-1	0.33	0.33	-1
3	1	-1	+1	0.33	0.33	-1
4	1	+1	+1	0.33	0.33	+1
5	1	0	0	-0.67	-0.67	0
6	1	+1	0	0.33	-0.67	0
7	1	-1	0	0.33	-0.67	0
8	1	0	+1	-0.67	0.33	0
9	1	0	-1	-0.67	0.33	0
$\sum_{u=1}^{N} x_{iu}^2$	9	6	6	2	2	4

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In order to get an orthogonal planning matrix [5], adjusted values of the level X' is introduced:

$$x_i' = (x_i)^2 - \frac{\sum_{u=1}^{N} x_{iu}^2}{N}$$
(1)

The extended planning matrix of the full factorial experiment (FFE) shown in Table 300 5.

Fable 5. The extended plar	ning matrix of the f	ull factorial experiment.
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	<i>q</i> , p	ts.wt.	E, GPa	W, kJ/m ²
	\boldsymbol{x}_1	X 2	y 1	y 2
1	60	10	5.8	8.5
2	80	10	4.0	7.3
3	60	30	5.5	8.1
4	80	30	4.4	7.4
5	70	20	5.0	8.3
6	80	20	4.6	7.6
7	60	20	5.5	8.7
8	70	30	4.6	8.2
9	70	10	5.4	8.0

The mathematical model $y = f(x_1, x_2)$ is made in the form of a regression equation:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2$$
(2)

Regression coefficients are determined using the following formula:

$$b_{i} = \frac{\sum_{u=1}^{N} x_{i} y_{i}}{\sum_{u=1}^{N} x_{iu}^{2}}$$
(3)

The obtained coefficients of the regression equation are shown in the Table 6.

Table 6. Coefficients of the regression equation.

b_0	b_I	b_2	b_{11}	b_{22}	b_{12}
5.06	-0.63	-0.12	-0.03	-0.08	0.18

The following regression equation is obtained when analyzing the modulus of elas-309 ticity during bending:

$$y = 5.06 - 0.63x_1 - 0.12x_2 - 0.03x_1^2 - 0.08x_2^2 + 0.18x_1x_2$$

For statistical processing of the obtained results of the experiment, a check of the re-311 producibility of the experiments is carried out according to the Cochrane's test:

$$G = \frac{S_{u \max}^2}{\sum_{u=1}^N S_u^2} \le G_{(0,05;f_1;f_2)}$$
(4)

where S^{2}_{ui} – dispersion that characterize the results of experiments on the <i>i</i> -th combination	313
of factor levels for $m = 3$;	314

n – the number of parallel experiments;	315
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- $S^{2}u \max$ the largest of the dispersions in the rows of the plan. 316
- Adequacy dispersion is determined by the following formula: 317

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$$S_{ui}^{2} = \frac{\sum_{i=1}^{m} (y_{i} - \overline{y_{i}})^{2}}{m-1}$$
(5)

where yim - value obtained from each parallel experiment;

yi – the average value obtained during parallel experiments. 319

The reproduction dispersion is determined by the following formula:

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$$\sigma^{2}\{y\} = \frac{\sum_{i=1}^{N=9} \sigma^{2}\{y\}_{i}}{N(m-1)}$$
(6)

where $\sigma^{2} \{y\}_{i} = \sum_{i=1}^{m=3} (y_{i} - \overline{y_{i}})^{2}$		321
	$s^{2} \{y\} = \frac{a^{2} \{y\}}{N}, \text{ or } S_{b_{0}}^{2} = \frac{S_{0}^{2}}{N}$ (7)	
		. 322

The value of dispersions is given in Table 7.

Table 7. Values of adequacy variance (S_{ui}^2) and reproduced variances ($\sigma^2 \{y\}_i$).

Dispersi		fadequacy	Dispersion of r	eproduction	
Nº	Conventional symbol	Value	Conventional symbol	Value	
1	S_{u1}^{2}	0.01	$\sigma^2 \{y\}_1$	0.02	
2	S_{u2}^2	0.01	$\sigma^2 \{y\}_2$	0.02	
3	S_{u3}^{2}	0.01	$\sigma^2 \{y\}_3$	0.02	
4	S_{u4}^{2}	0.03	$\sigma^2 \{y\}_4$	0.06	
5	S_{u5}^{2}	0.01	$\sigma^2 \{y\}_5$	0.02	
6	S_{u6}^2	0.03	$\sigma^2 \{y\}_6$	0.06	
7	S_{u7}^{2}	0.04	$\sigma^2 \{y\}_7$	0.06	
8	S_{u8}^{2}	0.01	$\sigma^2 \{y\}_8$	0.02	
9	S_{u9}^{2}	0.01	$\sigma^2 \{y\}_9$	0.02	

At the same time:

$\sum_{i=1}^{N} S_{ui}^2 = 0.15$	327
$\sigma^2 \{y\} = S_0^2 = 0.017$.	328

 $G = \frac{S_{u_{max}}^2}{\overset{N}{\underset{i=1}{\overset{N}{a}}}S_{ui}^2}$ (8)

$$G = \frac{0.03}{0.15} = 0.067.$$
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Checking the results of the experiment according to the Cochrane's test [5] for a fixed 331 probability $\alpha = 0.05$ confirmed the reproducibility of the experiments. Dispersion, which 332 characterizes the results of experiments on the i-th combination of factor levels: 333 $S_{umax}^2 = 0.03$. The calculated value of the Cochrane's test: G = 0.067. 334

Table value of Cochrane's test: $G_t = 0.478$. 335

That is, condition (7) is fulfilled:

$$G = 0.067 \le G_t = 0.478$$
 337

No of records	Elastic	ity modulus,	Average value,	
Nº 01 research	1	2	3	E, GPa
1	5.7	5.8	5.9	5.8
2	3.9	4.1	4.0	4.0
3	5.5	5.6	5.4	5.5
4	4.3	4.3	4.6	4.4
5	5.1	4.9	5.0	5.0
6	4.5	4.8	4.5	4.6
7	5.3	5.6	5.6	5.5
8	4.5	4.7	4.6	4.6
9	5.3	5.5	5.4	5.4

Table 8. Experimental results of the study of the elasticity modulus of CM.

Further, the significance of the coefficients of the regression equation is determined 338 by analyzing the results according to the experimental plan (Table 8). 339

Further, the dispersion of the regression coefficients (Table 9) are determined accord-343 ing to the following formula: 344

$$S_{b_i}^2 = \frac{S_0^2}{\sum_{i=1}^{N} x_{iu}^2}$$
(9)

The significance of the regression coefficients is determined by the Student's test [5]. 345 At the same time, the tabular (t_t) and calculated criterion (t_c) of Student's test are deter-346 mined (Table 9). 347

Depending on the degrees of freedom: f = N(n - 1) = 9(3 - 1) = 18, the tabular value of 348 the Student's test is determined, which is $t_t = 2.1$. 349

The calculated values of the Student's test (tc) and the significance of the coefficients are determined: *t*₀*c*, *t*₁*c*, *t*₂*c*, *t*₁₁*c*, *t*₂₂*c*, *t*₁₂*c* > *t*_t. 351

At the same time:

$$t_{ip} = \frac{|b_i|}{S_{b_i}};$$
(10)

Dispersions of regression coefficients Calculated values of Student's test N⁰ **Conventional symbol Conventional symbol** Value Value $S_{b_0}^2$ 1 0.002 116.63 t_{0p} $S_{b_{1}}^{2}$ 2 0.003 12.02 t_{1p} $S_{b_2}^2$ 3 0.003 2.21 t_{2p} $S_{b_{11}}^2$ 0.37 4 0.008 t_{11p} $S_{b_{22}}^2$ 5 0.008 0.91 t_{22p} $S_{b_{12}}^2$ 0.004 2.70 6 t_{12p}

Table 9. Dispersions of regression coefficients (S_t^2) and calculated values of Student's test (t_c).

The calculated values of the Student's test t_{0cr} , t_{1cr} , t_{2cr} , t_{12c} are greater than t_{tr} , so it is 355 considered that the coefficients of the regression equation b_0 , b_1 , b_2 , b_{12} are significant. The 356 calculated values of t_{11c_1} t_{22c} are smaller than tt, so the coefficients b_{11} , b_{22} are not significant. 357

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As a result of discarding insignificant coefficients, the following regression equation is 358 obtained: 359

$$y = 5.06 - 0.63x_1 - 0.12x_2 + 0.18x_1x_2$$
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The adequacy of the obtained model is checked according to Fisher's test [39]:

$$F_{p} = \frac{S_{u}^{2} max}{S_{y}^{2}} \pounds F_{(0.05; f_{a\partial}; f_{y})}$$
(11)

where $S_{u \max}^2 = 0.03$ – the calculated value of the dispersion of adequacy (Table 7):

$$S_{y}^{2} = \frac{\sum_{i=1}^{N} S_{ui}^{2}}{N};$$
(12)

 $S_{y^2} = 0.017$ – dispersion of reproduction.

Then: $F_c = 0.6$.

 $F_{(0,05;f_{a0};f_{u})} - \text{tabular value of Fisher's test at the 5\% level of significance } (f_1 = N - (k + 365 + 1) = 9 - (4 + 1) = 4, f_2 = N (n - 1) = 9 (3 - 1) = 18). \text{ Then: } F_{(t)} = 2.93 [39].$

The calculated value of Fisher's test is smaller than the table value, that is, condition 367 (10) is fulfilled. It can be assumed that the equation adequately describes the composition 368 formulation. 369

The process of interpreting the obtained mathematical model, as a rule, is not reduced only to determining the influence of factors. A simple comparison of the absolute value of the linear coefficients does not determine the relative degree of influence of the factors, since there are also quadratic terms and pairwise interactions. In the detailed analysis of the obtained adequate model, it is necessary to take into account the fact that for the quadratic model the degree of influence of the factor on the change of the initial value is not constant. 370 371 372 373 374 375

Dependencies connecting normalized and natural values of variable factors have the following form: 377

$$x_i = \frac{q_i - q_{i0}}{\Delta q_i} \tag{13}$$

where q_i – value of the *i*-th factor of the experiment,

*q*ⁱ⁰ – zero level value,

 Δq_i – variation interval [5].

Substituting these values according to formula (13) into the regression equation and transforming it, we obtain the following regression equation with the natural value of the variable parameters: 384

$$E = 12.23 - 0.099q_1 - 0.138q_2 + 0.0018q_1q_2$$

$$385$$

The given equation in natural values allows only to predict the value of the initial 386 value for any point in the middle of the factor variation area. However, with its help, it is 387 possible to plot graphs of the dependence of the initial value (modulus of elasticity during 388 bending of composites) on any factor (or two factors). The geometric interpretation of the 389 response surface is shown in Fig. 1-3. 390

Based on experimental studies, it is established that both factors are significant. It 391 should be noted that the influence of the content of the main filler on the indicators of the 392 elastic modulus during bending is higher compared to the additional one (according to 393 the Pareto map). Analyzing the calculated response surface, it is determined that the de-veloped epoxy composite with a two-component polydisperse filler with the following 395 particle content: iron slag – 60–70 wt%, Waltrop – 10–20 wt%, has the optimal indicators 396 of the modulus of elasticity during bending (E = 5.5-5.8 GPa). 397

Similar to the above scheme of calculations, the composition of CM is optimized according to the impact viscosity indicators. The coding of the natural values of the 399

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components and the scheme of planning the experiment are selected according to Tables 400 3 and 4. 401

In the process of analyzing the results of the study of impact resilience of composites, regression coefficients are obtained and presented in Table 10.







Figure 2. Calculated response surface $E = f(q_1, q_2)$.



Figure 3. Contours of the calculated response surface.

In the process of analyzing the results of the study of impact resilience of composites, 410 regression coefficients are obtained and presented in Table 10. 411

Table 10. Coefficients of the regression equation for impact resilience.

b_0	b_1	b_2	b_{11}	<i>b</i> ²²	b_{12}
8.36	-0.50	-0.02	-0.23	-0.28	0.13

As a result, the following regression equation is derived: $y = 8.36 - 0.50x_1 - 0.02x_2 - 0.23x_1^2 - 0.28x_2^2 + 0.13x_1x_2$ 414
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For statistical processing of the obtained results of the experiment, the reproducibility of the experiments is checked according to the Cochrane's test [5]. 417

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Values of dispersions, which are determined by Equations 5 to 7, are given in the 418Table 11. 419

					_
	Adequacy dis	persion	Reproduction	dispersion	
N⁰	Conventional sym- bol	Value	Conventional symbol	Value	
1	S_{u1}^2	0.01	$\sigma^2 \{y\}_1$	0.02	
2	S_{u2}^{2}	0.07	$\sigma^2 \{y\}_2$	0.14	
3	S_{u3}^{2}	0.04	$\sigma^2 \{y\}_3$	0.08	
4	S_{u4}^{2}	0.07	$\sigma^2 \{y\}_4$	0.14	
5	S_{u5}^{2}	0.03	$\sigma^2 \{y\}_5$	0.06	
6	S_{u6}^{2}	0.01	$\sigma^2 \{y\}_6$	0.02	
7	S_{u7}^{2}	0.04	$\sigma^2 \{y\}_7$	0.08	
8	S_{u8}^{2}	0.03	$\sigma^2 \{y\}_8$	0.06	
9	S_{u9}^{2}	0.01	$\sigma^2 \overline{\{y\}_9}$	0.02	

Table 11. Adequacy dispersion value (S_u^2) and reproduction dispersion value ($\sigma^2(y)$).

At the same time:

$$\sum_{i=1}^{N} S_{ui}^{2} = 0.31, \quad \sigma^{2} \{y\} = S_{0}^{2} = 0.034$$
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Then the calculated value of the Cochrane's test at the 5% level of significance is de-424 termined by Equation (8):

$$G_p = \frac{0.07}{0.31} = 0.226$$

Checking the results of the experiment according to the Cochrane's test [5] for a fixed 426 probability α = 0.05 confirmed the reproducibility of the experiments. Dispersion, which 427 characterizes the results of experiments on the *i*-th combination of factor levels: 428 $S_{u \text{max}}^2 = 0.07$. Calculated value of Cochrane's test: G = 0.226. 429

Table value of Cochrane's test: $G_t = 0.478$. 430

That is, the condition is fulfilled:

$$G = 0.226 \le G_t = 0.478$$

At the next stage, the significance of the coefficients of the regression equation is de-432 termined, analyzing the results according to the experimental plan and presented in Table 433 12. 434

Table 12. Experimental results of the study of impact resilience of CM.

№ of the experi-	Impact resilience, <i>W</i> , kJ/m ²		Average value,	
ment	1	2	3	<i>W</i> , kJ/m ²
1	8.4	8.5	8.6	8.5
2	7.0	7.5	7.4	7.3
3	7.9	8.3	8.1	8.1
4	7.2	7.7	7.3	7.4

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5	8.1	8.4	8.4	8.3
6	7.6	7.7	7.5	7.6
7	8.9	8.5	8.7	8.7
8	8.0	8.3	8.3	8.2
9	8.0	8.1	7.9	8.0

Equations 9 and 10. The significance of the regression coefficients is determined by 437 the Student's test, the tabular value of which is $t_t = 2.1$ [39]. The calculated values of the 438 Student's test are given in the Table 13. 439

Table 13. Dispersions of regression coefficients (S_h^2) and calculated values of Student's test (t_c).

Nº -	Dispersions of regression coefficients		Calculated values of Student's test	
	Conventional symbol	Value	Conventional symbol	Value
1	$S_{b_0}^2$	0.004	t_{0p}	132.44
2	$S_{b_{\mathrm{l}}}^{2}$	0.006	t_{1p}	6.60
3	$S_{b_2}^2$	0.006	t_{2p}	0.22
4	$S_{b_{11}}^2$	0.017	t_{11p}	1.78
5	$S_{b_{22}}^{2}$	0.017	t_{22p}	2.16
6	$S_{b_{12}}^2$	0.009	t_{12p}	1.30

The calculated values of the Student's test t_{0c} , t_{1c} , t_{2c} are greater than t_t , so it is consid-442 ered that the coefficients b_0 , b_1 , b_2 of the regression equation are significant. The calculated 443 values of t_{11c} , t_{22c} , t_{12c} are smaller than t_i , so the coefficients b_{11} , b_{22} , b_{12} are not significant. As 444 a result, the following regression equation is obtained: 445

$$y = 8.36 - 0.50x_1 - 0.28x_2^2$$

The adequacy of the obtained model is checked according to Fisher's test [5]. 446 Calculated value of dispersion of adequacy: $S_{u \max}^2 = 0.07$ (Table 11). 447

Reproducibility dispersion: $S_y^2 = 0.034$.

Then: F = 2.032.

 $F_{(0,05;f_W;f_u)}$ – tabular value of Fisher's test at the 5% level of significance ($F_{(t)}$ = 2.77) [39]. 451

The calculated value of Fisher's test is smaller than the table value, that is, condition (11) is fulfilled. Therefore, the equation adequately describes the composition formulation. 453

After carrying out the transformation according to formula (13), the following regres-454 sion equation with the natural value of the variable parameters is obtained: 455

$$W = 10.74 - 0.05q_1 + 0.112q_2 - 0.0028q_2^2$$

The geometric interpretation of the response surface is shown in Figs 4 to 6.

The obtained results indicate that both factors of the regression equation are signifi-457 cant. It should be noted that the initial parameters of the composite are affected by the 458 linear dependence of the first factor and the quadratic dependence of the second. In the 459 process of analysis, it is established that the impact resilience indicators take their maxi-460 mum values with the content of fillers: iron slag – 60-70 wt%, Waltrop – 10-20 wt% (W = 461 $8.5-8.7 \text{ kJ/m^2}$). With a further increase in the content of particles, a deterioration of the 462 impact resilience indicators is observed. This may be is a consequence of the aggregation 463 of fillers in the polymer matrix, which negatively affects the physical and mechanical 464

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properties of the material. Therefore, it is advisable to introduce the two-component pol-465ydisperse filler with the above-mentioned content into the modified epoxy matrix to im-466prove the operational characteristics during the repair of elements of transport means.467





So, by the method of mathematical planning of the experiment, the critical content of 470 the two-component polydisperse filler is established: iron slag ($d = 60-63 \mu m$) – 60–70 wt%, 471 Waltrop ($d = 8-10 \mu m$) – 10–20 wt% per 100 wt% of epoxy oligomer ED-20. The introduc-472 tion of the two-component polydisperse filler into the epoxy binder makes it possible to 473 significantly increase the indicators of the elastic modulus during the bending of protec-474 tive coatings to E = 5.5-5.8 GPa and the impact resilience to W = 8.5-8.7 kJ/m². The obtained 475 results make it possible to create materials with improved overall indicators of physical 476 and mechanical properties. It is advisable to use the obtained materials in the form of 477 protective coatings to improve operational characteristics and repair parts of transport 478 equipment. 479



Figure 5. Calculated response surface $W = f(q_1, q_2)$.



Figure 6. Contours of the calculated reference surface.

Therefore, introducing a two-component polydispersed filler into the epoxy binder 484 allows significantly increasing the indicators of the modulus of elasticity during bending 485 of protective coatings from E = 4.0...44 GPa (composites containing one filler) to 486

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E = 5.5...5.8 GPa and impact viscosity from W = 7.7...8.2 kJ/m² (composites containing one filler) to W = 8.5...8.7 kJ/m².

3.2. The results of the study of the corrosion resistance of polymer CM

The development of industry creates the conditions for the creation of new materials 490 with increased operational characteristics in the complex. At the same time, the anti-cor-491 rosion properties of protective composite coatings (CC), as well as the wear resistance of 492 finished products, are of great importance. In this context, the use of epoxy-based polymer 493 CCs is effective. Such materials are characterized by improved thermophysical, physico-494 mechanical, adhesive properties and minor residual stresses [40-44]. The predicted control 495 of the technological methods of introducing ingredients of different activity, dispersion, 496 and nature under critical content at the initial stage of the formation of compositions will 497 allow the formation of protective coatings with improved anti-corrosion properties [45, 498 46]. 499

The analysis of existing publications in the direction of researching the properties of 500 epoxy CMs indicates the need to introduce plasticizers, modifiers, and fillers into the 501 binder to obtain epoxy polymers with increased operational characteristics. It is proven 502 [47-50] that the introduction of modifiers and dispersed particles into the binder, even in 503 small quantities, ensures a change in the speed of the physicochemical processes during 504 the structuring of CM. Moreover, not only the chemical and physical nature but also the 505 content and dispersion of the particles are important in regulating the crosslinking pro-506 cesses of epoxy CMs. As stated in works [36, 51], it is advisable to introduce finely dis-507 persed particles (8–30 µm) into the binder to improve the adhesive properties, and it is 508 necessary to use a dispersed filler (63–120 μ m) to improve the cohesive strength of com-509 posites. Taking this into account, it is considered expedient to conduct relevant studies to 510 establish the influence of the nature of nano- and microdisperse fillers on the anti-corro-511 sion properties of epoxy CMs. 512

Developed protective coatings based on a modified epoxy binder with a three-component dispersed filler, the content of which is determined as a result of previous researches, are studied for anti-corrosion protection of technological equipment that is operated in aggressive environments, (Table 4). 516

Five compositions of anti-corrosion coatings are tested:

- matrix (control sample) (the matrix is formed using the following ratio of components epoxy oligomer ED-20: hardener PEPA 100: 10);
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- CM 1 (the composite is formed according to the following ratio of components matrix: nanopowder, which is a mixture of nanodispersed compounds (MNDC) (30–90 521 nm): iron scale (IS) (60–63 μm): Waltrop (WT) (8–12 μm) 100 : 0.25 : 70 : 10); 522
- CM 2 (the composite is formed according to the following ratio of components binder: MNDC : IS : WT – 100 : 0.25 : 60 : 20);
- CM 3 (the composite is formed according to the following ratio of components binder: MNDC : IS : Agocel S-2000 (AC) (8–12 μm) – 100 : 0.25 : 60 : 30);
- CM 4 (the composite is formed according to the following ratio of components binder: MNDC : IS : AC – 100 : 0.25 : 70 : 20).

It is experimentally established that water sorption by epoxy composites significantly 529 depends on the nature and cohesive strength of the coatings (Fig. 7). It is found that com-530 posites filled with iron slag and Waltrop particles are the most waterproof, and composites 531 containing iron slag particles and Agocel S-2000 are characterized by significant water 532 sorption. The obtained results are in good agreement with the results of testing the cohe-533 sive properties of the investigated coatings – the highest water resistance is observed in 534 coatings with significant cohesive strength and insignificant indicators of residual 535 stresses. It is established that at the initial stage of the study (up to 150 days) intensive 536 swelling of all protective coatings is observed without exception. It is assumed that the 537

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aggressive environment penetrates not only into the surface layer of coatings, but also into 538 their volume. As a result, at this stage of research, the relative mass of protective coatings 539 is $\chi = 0.5-1.2$ %. It is proven (Fig. 7) that samples from the epoxy matrix have the maximum 540 permeability ($\chi = 1.8$ %) during the determined interval of the study (t = 150 days). In our 541 opinion, the obtained results are due to intensive penetration of molecules of an aggres-542 sive environment not only into the volume of the polymer, but also into the metal base. At 543 the same time, the "polymer-substrate" connections are replaced by "environment-sub-544 strate". It is known [10] that adhesive bonds in such a tense state eventually break down, 545 forming microcracks, since, according to the Rebinder wedging effect, an aggressive envi-546 ronment, penetrating the crack, causes its further development. Compared to the studied 547 protective coatings, the original epoxy matrix is characterized by the lowest indicators of 548 adhesive and cohesive strength, as well as significant residual stresses. As a result of the 549 penetration of an aggressive environment into the volume of the polymer at the initial 550 stage, its swelling occurs, later, according to the Rebinder effect, microcracks are formed, 551 and then a network of macrocracks. This, in turn, leads to the intensification of the swell-552 ing process, which is observed mainly during the time t = 50-100 days of the study. 553

Further analysis of the research results allows stating that during the time t = 150...300 554 days of the study, the relative mass of the samples (CC 1–CC 4) practically does not change 555 (the values are within the experimental error). However, it should be noted that during 556 this research period, the relative mass of samples from the original epoxy matrix increases 557 from $\chi = 1.8$ to $\chi = 1.9\%$. This indicates the continuation of the process of penetration of 558 an aggressive environment into the polymer, which leads to further destruction of chemical bonds and, as a result, peeling of the coating from the base. 560



Figure 7. Dependence of water sorption in natural conditions by protective coatings on duration 562 of exposure: 1 – matrix (control sample); 2 – CC 1; 3 – CC 2; 4 – CC 3; 5 – CC 4. 563

A comparative analysis of the behavior of the studied composites (CC 1–CC 4) under 564 the influence of an aggressive environment in natural conditions allows stating that the 565 rate of water diffusion into the polymer composite is determined mainly by diffusion at 566 the "polymer-filler" separation boundary. It is previously proven that CC 1 and CC 3 ma-567 terials have the best indicators of adhesive and cohesive strength among all the studied 568 materials. It is established (Fig. 7) that the protective coating filled with particles of a mix-569 ture of nanodispersed compounds (30–90 nm) (q = 0.25 wt%), iron scale (60–63 µm) (q = 70570 wt%) and Waltrop (8–12 μ m) (q = 10 wt%) has the lowest permeability indicators. The 571 permeability in natural conditions of such a coating during the time t = 250-300 days of 572 the study is $\chi = 0.5\%$, which is 3.6 times less than the similar indicators of the epoxy matrix. 573 This is due to the increased cohesive and adhesive strength of the developed coating to 574 the metal base, which is decisive in the formation of adhesives with improved anti-corrosion properties. 575

It is interesting from a scientific and practical point of view to conduct additional 577 studies of the corrosion resistance of the developed materials in various aggressive environments. Therefore, in order to confirm the above results, the permeability of the composites is tested in the following enviroments: gasoline, acetone, NaOH (50%), I-20A lubricant and H₂SO₄ (10%) (fig. 8, a-f). 581



Figure 8. Determination of permeability index in aggressive environments: a – sulfuric acid (CAS 583 No. 7664-93-9); b – solutions of sodium (CAS No. 1310-73-2); c – technical water (CAS No. 7732-18-5); d – gasoline (CAS No. 64742-82-1); e – acetone (CAS No. 67-64-1); f – I-20A lubricant (CAS No. 585 64742-62-7).

The results of experimental studies show the high chemical stability of materials 587 based on an epoxy binder in various aggressive environments. It is established that the 588 most aggressive environment for the polymer matrix is a solution of sulfuric acid (Table 589 14). This is due to the fact that the significant destruction of the matrix in the acid solution 590 occurs due to the sorption of the components of the aggressive environment by the polymer, while the structure of the matrix changes and the physical and chemical bonds destroy. 593

It is established (Table 14) that the introduction of dispersive fillers into the epoxy 594 oligomer helps to increase the chemical resistance of the materials. This is due to a de-595 crease in the relative content of the polymer in the volume of the composite and an in-596 crease in the path of penetration of molecules of corrosive agents during diffusion to the 597 metal base due to the barrier effect created by the dispersed particles of the filler. The 598 obtained results of materials research in aggressive environments correlate with similar 599 results of tests of the same composites in natural conditions. It is established (Table 14) 600 that the CC 1 composite has the best indicators of chemical resistance among all the stud-601 ied materials. It is proven that the formation of an epoxy-based coating with particles of 602 iron slag and Waltrop at the optimal content (respectively, q = 70 wt% and q = wt% for q =603 100 wt% of ED-20 resin) increases relative to epoxy matrix indicators of chemical re-604 sistance: 2.9 times in gasoline; 3.3 times in acetone; 2.9 times in NaOH (50%); 2.9 times in 605 I-20A lubricant; 2.0 times in $H_2SO_4(10\%)$. First of all, this is due to the cohesive interaction 606 at the "polymer-filler" phase separation boundary, which significantly affects the protec-607 tive properties of CC. Low adhesion of dispersed particles to the polymer in the volume 608 of the coating reduces the protective properties of the adhesive due to the development of 609 a network of cracks, which, in most cases, is associated with the dislodging effect of an 610 aggressive environment. 611

Composites filled with iron scale and additionally Agocel S-2000 particles have low 612 chemical resistance, especially in I-20A lubricant and in NaOH and H₂SO₄ solutions. This 613 is due to the adsorption of water and molecules of active reagents on the surface of hydrophilic oxides in the form of hydroxyl groups held by hydrogen bonds. 615

Turna of	Aggressive enviroment					
coating	Gasoline	Acetone	NaOH (50 %)	I-20A lubricant	H2SO4 (10 %)	
Matrix	5.2	5.0	5.3	6.3	8.4	
CC 1	1.8	1.5	1.8	2.2	4.3	
CC 2	2.4	2.8	2.6	3.2	5.5	
CC 3	1.9	1.9	2.2	2.8	5.0	
CC 4	2.7	2.8	2.9	3.6	6.1	

Table 14. Relative change in mass (χ , %) of composites after their aging in aggressive environments616(at temperature $T = 293 \pm 2$ K, during $\tau = 1420$ h).617

Therefore, modified epoxy composite protective coatings with improved anti-corrosion properties are developed in the work. 620

- It is established that the protective coating filled with particles of a mixture of nano-1. 621 dispersed compounds (30–90 nm) (q = 0.25 pts.wt.), iron scale (60–63 μ m) (q = 70622 pts.wt.) and Waltrop (8–12 μ m) (q = 10 pts.wt.) has the lowest permeability indicators. 623 The permeability in natural conditions of such a coating during the time t = 250-300624 days of the study is $\chi = 0.5\%$, which is 3.6 times less than the similar indicators of the 625 epoxy matrix. This is due to the increased cohesive and adhesive strength of the de-626 veloped coating to the metal base, which is decisive in the formation of adhesives 627 with improved anti-corrosion properties. 628
- 2. It is proven that the formation of an epoxy-based coating with particles of iron slag and Waltrop at the optimal content (respectively, q = 70 pts.wt. and q = 10 pts.wt. for q = 100 pts.wt. of ED-20 resin) increases relative to the initial chemical resistance indicators of the epoxy matrix: 2.9 times in gasoline; 3.3 times in acetone; 2.9 times in NaOH (50%); 2.9 times in I-20A lubricant; 2.0 times in H₂SO₄ (10%). This is due to the cohesive interaction at the "polymer – filler" phase separation boundary, which significantly affects the protective properties of the adhesive.

3.3. The results of the study of hydroabrasive wear resistance of polymer CMs

At the next stage, the wear resistance of the developed materials under the action of hydroabrasive is investigated (fig, a-f). 638

The analysis of the coefficient of wear resistance of the studied CMs at the angle of 639 attack of the hydroabrasive mixture $a = 45^{\circ}$ allows stating that the wear resistance is rela-640 tively high in all, without exception, samples. It is experimentally established that the in-641 itial epoxy matrix has the lowest coefficient of wear resistance among all investigated com-642 posites (Fig. 10). It is shown that at the angle of attack of the hydroabrasive $a = 45^\circ$, the 643 wear resistance coefficient of the matrix is K = 1.32. The authors [11, 24, 52-54] proved that 644the intensity of wear depends on various destruction processes: knocking out the coating 645 surface with an abrasive mixture and its deformation. At the same time, the dominant 646 influence of each of the processes depends on the cohesive strength of the CM. The method 647 of optical microscopy proved that the matrix is characterized by two types of destruction 648 of the surface layer of the material: macrocutting and plastic deformation with subsequent 649 removal of the material. 650

Additionally, it is established (Fig. 8) that the CC 3 composite is characterized by the highest indicators of resistance to hydroabrasive operation, for which the following indicator of wear resistance is observed – K = 1.75. It is confirmed by the method of optical microscopy that branched relief bands are observed on the surface of such a composite, which arose as a result of the action of water abrasive particles (Fig. 11, a). At the same time, compared to the matrix, they are not so deep, and their length is much shorter. The improvement in the wear resistance of epoxy composites can be explained by their 657

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improved cohesive properties compared to the epoxy matrix, which implies an increase 658 in the wear resistance coefficient. 659

Figure 9. General appearance of the formed samples used in the study of hydroabrasive wear660resistance: a - epoxy matrix; b - CC 1; c - Ct 3 steel; d - CC 2; e - CC 3; f - CC 4.661

Composites filled with particles of iron slag and Waltrop (CC 1, CC 2) are character-662 ized by slightly worse indicators of wear resistance. It is proved (Fig. 10) that at the angle 663 of attack of hydroabrasive $a = 45^\circ$, their wear resistance increases in relation to the matrix 664 from K = 1.32 to K = 1.54 - 1.68. At the same time, the course of the process of knocking out 665 the surface of the coating with an abrasive mixture is observed, which is typical for the 666 wear of fragile heterogeneous polymer composites. The method of optical microscopy 667 confirmed (Fig. 11, b, c) that multiple deformations of CM as a result of micro-impacts by 668 abrasive particles lead to the formation of micro-cracks on the surface, the plane of which 669 is perpendicular to the direction of movement of the water-abrasive mixture. In this case, 670 grooves appear on the contact surface, which have an orientation in the direction of the 671 sliding speed vector of the hydroabrasive flow [55-57]. Mostly, such a mechanism makes 672 an insignificant contribution to the activation process, compared to the mechanism of plas-673 tic deformation, which is dominant for epoxy matrix. When implementing such a trigger 674 mechanism, individual abrasive particles under the influence of a significant nominal 675 pressure of the hydroabrasive flow are wedged into the surface layer of the CM, plastically 676 deforming the epoxy matrix. As a result, an area of compressive deformation (in front of 677 the contact area) and tensile deformation (behind the contact area) is formed, which leads 678 to the formation of different sizes of microcracks. Under the influence of the tangential 679 force of the hydroabrasive flow, the abrasive particle together with part of the polymer is re-680 moved from the surface of the material. Multiple deformation of polymer composites con-681 taining dispersed particles as a result of subsequent activation leads to fatigue and local 682 removal of the epoxy composite. This leads to the formation of new microcracks. Over 683 time, the destruction is localized in those areas of the CM that have the highest density of 684 microcracks. At the same time, it is possible to expect the appearance of a macrocrack ori-685 ented perpendicular to the direction of the speed of movement of the water-abrasive 686 mixture. Under the influence of repeated maximum deformations, there is an increase in 687 macro-destroyed areas with removed polymer, which leads to the formation of a wavy 688 relief called the "Shallomach pattern". The waves observed by optical microscopy on the 689 surface of CM samples (Fig. 11, b, c) are located perpendicular to the direction of move-690 ment of the abrasive particles, and the pattern of the triggering surface is preserved even 691 after repeated studies. 692



Figure 10. Dependence of the coefficient of wear resistance (K) at the angle of attack of the hydroa-694 brasive $a = 45^{\circ}$ on the content and nature of the ingredients in the composites: No.1 – matrix (control 695 sample); No. 2 – CC 1; No. 3 – CC 2; No. 4 – CC 3; No. 5 – CC 4.





Figure 11. Appearance of the surface after hydroabrasive destruction of CM containing: a) CC 3; b) 698 CC 1; c) CC 2. 699

So, according to the test results, it is established that the protective coating filled with 700 particles of a mixture of nanodispersed compounds (30-90 nm) (q = 0.25 wt%), iron scale 701 $(60-63 \ \mu\text{m})$ (*q* = 60 wt%) and Agocel S-2000 (8–12 μm) (*q* = 30 wt%) have the highest indi-702 cators of wear resistance. The coefficient of wear resistance under the action of hydroabra-703 sive of such a coating is K = 1.75, which is 1.3 times higher than the similar indicators of 704 the epoxy matrix. It is shown that the mechanism of wear of materials is determined by 705

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physical and mechanical processes on the surface of composites, the determining factors 706 of which are the processes of knocking out microparticles of the surface of the coating 707 with an abrasive mixture and the formation of a wavy relief. 708

In addition, SEM images of the structure of the studied CMs are provided in the work 709 for a detailed analysis of the structure of the formed materials. It is considered appropriate 710 to present the results of the study of the structure of the CM, which are shown in Fig. 11, 711 i.e. CC 3, CC 1 and CC 2. 712

The analysis of the SEM image of the fracture surface of CC 3 deserves special atten-713 tion (Fig. 12, a). Such coatings are characterized by a finer and more uniform topology of 714 the fracture surface, which makes it possible to assume the presence of stoppers for the 715 propagation of microcracks, through which particles of nano- and microfillers can protrude in a uniformly structured system "polymer - dispersed particles". Due to the organization of the nanolevel system of microcrack stoppers, the energy expended on the destruction of materials increases (Fig. 10, Fig. 11). At the same time, indicators of the coeffi-719 cient of hydroabrasive wear resistance of CM are increasing. It can be argued that the 720 propagation of main cracks, which originate at the point of impact of hydroabrasive par-721 ticles, is inhibited, which further confirms the above statements. 722

Analysis of the SEM image of the fracture surface of the CC 1 material (Fig. 12, b) similarly revealed a fine but heterogeneous topology of the fracture surface.

Additionally, the fracture surface of the CC 2 material is analyzed (Fig. 12, c). Analy-725 sis of the SEM image revealed the inhomogeneity of the veneers with the chaotic direction 726 of crack propagation, which indicates the instability of the operational characteristics of 727 such materials.







b)

Figure 12. Electron micrographs of the structure of epoxy composites: a) CC 3; b) CC 1; c) CC 2 730

3.4. Protective epoxy composite coatings with increased operational characteristics for the repair of parts of transport equipment 732

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On the basis of the conducted research, materials and modes of formation of epoxy compositions for protective coatings with increased operational characteristics are developed. The developed polymer composite coatings (PCC) that meet high operational requirements include: PCC-1, PCC-2. 736

Coating 1 (PCC-1). The main purpose of the coating is to improve the anti-corrosion 737 properties of technological equipment. PCC-1 is a material based on epoxy matrix, nanoand microdispersed filler. The developed material has high performance characteristics 739 and anti-corrosion properties, and its service life is 3–5 years. The low cost of the ingredients of the polymer composition, compared to known materials, is ensured by the increase 741 in quality and the increase in the service life and inter-repair periods of work. 742

The technological process of forming PCC-1 consists of the following operations: surface preparation, preparation of compositions, application of adhesive and surface layers, polymerization of the material. 743

The quality of preparation of the protective surface largely determines the reliability and durability of PCC-1. Surface preparation consists in degreasing and removal of various impurities, scale, and rust by sandblasting.

Preparation of compositions consists in dosing of components and preparation of fillers (purification of dispersed particles from impurities by ultrasonic treatment). Powders of homogeneous fractions are dried in an oven at a temperature of 353–363 K for 2 hours. 752

Fillers are added to the epoxy resin in appropriate proportions and mixed. After hydrodynamic mixing of the components, the hardener is introduced immediately before applying the composition to the steel surface. 753

Coating 1 (PCC-1) consists of the following components, pts.wt.:		756
- epoxy dian oligomer ED-20	100	757
- hardener polyethylene polyamine (PEPA)	10	758
- filler:		759
- nanodispersed filler in the form of a mixtureof nanodi	spersed compounds (Si ₃ N ₄ ,	760

- nanodispersed filler in the form of a mixtur	reof nanodispersed compounds (Si3N4,
I2O3, Al2O3) (MNDC), (30–90 nm)	0.25-0.50
- Waltrop (WT), (8–12 μm)	10–20
- iron scale (IS), (60–63 μm)	60–70

The coating is applied in traditional ways. The most productive and technological 764 method is the method of pneumatic spraying, which allows applying uniform layers of 765 material on the surface of a complex configuration. 766

Coating 2 (PCC-2). The main purpose is to increase the resistance to hydroabrasive 767 operation of technological equipment. The developed material has high physical, mechan-768 ical, thermophysical properties, and wear resistance, and its service life is 4–6 years. 769

The technological process of forming PCC-2 consists of the operations given above when describing the technology of forming the cover of PCC-1. After hydrodynamic mixing of the components, the hardener is introduced immediately before applying the composition to the steel surface.

Coating 2 (PCC-2) consists of the following components, pts.wt.:

- epoxy dian oligomer ED-20	100
- hardener polyethylene polyamine (PEPA))	10

- filler:

 - nanodispersed filler in the form of a mixture of nanodispersed compounds
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 (Si₃N₄, I₂O₃, Al₂O₃) (MNDC), (30–90 nm)
 0.10–0.25
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 - Agocel S-2000 (AC), (8–12 μm)
 20–30
 780

 - iron scale (IS), (60–63 μm)
 60–70
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The coating is applied by the method of pneumatic spraying, which allows forming 782 uniform layers of material on the surface of a complex configuration. 783

The results of comparative tests of physico-mechanical, thermo-physical, anti-corrosion properties, and resistance to hydroabrasive action of developed materials and 785 protective coatings based on them testify to high operational characteristics and the feasi-786 bility of using new composites for the repair of equipment, sea and river transport (Table 15).

Table 15. Comparative indicators of properties of developed composite materials and coatings 789 based on them. 790

Indicator	PCC-1	PCC-2
Adhesive strength (σ_a , MPa)	53	53
Destructive stresses during bending (σ_{bd} , MPa)	54	56
Modulus of elasticity in bending (E, GPa)	5.8	5.3
Heat resistance (<i>T</i> , K)	364	366
Impact resilience (W, kJ/m ²)	8.7	8.2
Penetration in natural conditions of the coating during time $t = 250-300$ days (χ %)	0.5	0.7
Wear resistance (at the angle of attack of hydroabrasive $a^{a} = 45^{\circ}$), <i>K</i>	1.68	1.75

4. Conclusions

This paper developed a new approach to solving an important scientific and technical 792 problem, which consists of the development of modified and filled with nano- and microdispersed particles protective coatings with increased operational characteristics for the restoration of transport. The solution to the scientific problem consists of scientifically based management of the processes of interphase interaction as a result of the predicted 796 introduction of additives into the binder at an optimal content, as well as in establishing 797 the regularities of the interrelationship of anti-corrosion properties and wear resistance 798 with the structure of materials. As a result of the work, the following main conclusions 799 are obtained: 800

A mathematical model is developed for optimizing the content of components in the 801 formation of protective anti-corrosion and wear-resistant coatings for means of transport 802 as a result of the complex effect of a mixture of nanodisperse compounds, iron scale and 803 Waltrop. Using the method of mathematical planning of the experiment using the STAT-804 GRAPHICS® Centurion XVI application package, the content of additives of different 805 physical and chemical nature in the epoxy binder is optimized to obtain protective coat-806 ings with improved operational characteristics. It is proved that the introduction of iron 807 scale ($d = 60...63 \mu$ m) – 60...70 pts.wt. and Waltrop ($d = 8...12 \mu$ m) – 10...20 pts. wt. per 100 808 pts. wt. of oligomer ED- 20 and 10 pts. wt. of the PEPA hardener ensures the formation of 809 a material with a bending modulus of elasticity -E = 5.5...5.8 GPa and an impact resilience 810 -W = 8.5...8.7 kJ/m². That is, optimization of the content of fillers of different physical and 811 chemical nature in the epoxy binder provides a 1.3 increase in physical and mechanical 812 properties (compared to an unfilled matrix), which makes it possible to use such materials 813 in the formation of functional protective coatings. 814

Modified epoxy composite protective coatings with improved anti-corrosion proper-815 ties and wear resistance under hydroabrasive conditions are developed. It is established 816 that the protective coating filled with particles of a mixture of nanodispersed compounds 817 (30-90 nm) (*q* = 0.25 wt%), iron scale (60–63 µm) (*q* = 70 wt%) and Waltrop (8–12 µm) (*q* = 818 10 wt%) has the lowest permeability indicators. The permeability in natural conditions of 819 such a coating during the time t = 300 days of the study is $\chi = 0.5\%$, which is 3.6 times less 820 than the similar indicators of the epoxy matrix. A comparative analysis of the behavior of 821 the studied composites under the influence of an aggressive environment in natural con-822 ditions allows stating that the rate of diffusion of water into the polymer composite is 823 determined mainly by diffusion at the border of the "polymer – filler" separation. It is 824 previously proven that the material of this composition has the best indicators of adhesive 825

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and cohesive strength among all the studied materials. This is due to the increased cohesive and adhesive strength of the developed coating to the metal base, which is decisive 827 in the formation of adhesives with improved anti-corrosion properties. 828

It is proven that the formation of an epoxy-based coating with particles of iron slag 829 and Waltrop at the optimal content (respectively, q = 70 wt% and q = 10 wt% for q = 100830 wt% of ED-20 resin) increases relative to the initial indicators of chemical resistance of the 831 epoxy matrix: 2.9 times in gasoline; 3.3 times in acetone; 2.9 times in NaOH (50%); 2.9 832 times in I-20A lubricant; 2.0 times in H2SO4 (10%). First of all, this is due to the cohesive 833 interaction at the boundary of the "polymer - filler" phase separation, which significantly 834 affects the protective properties of the coating. The high adhesion of dispersed particles 835 to the polymer in the volume of the coating increases the protective properties of the ad-836 hesive due to a decrease in the rate of development of the crack network. The latter, in 837 most cases, is associated with the disintegrating effect of an aggressive environment. 838

It is substantiated that the protective coating filled with particles of a mixture of nano-839 dispersed compounds (30–90 nm) (q = 0.25 wt%), iron scale (60–63 microns) (q = 60 wt%) 840 and Agocel S-2000 (8–12 μ m) (q = 30 wt%) is characterized by the highest indicators of 841 wear resistance. The coefficient of wear resistance under the action of hydroabrasive of 842 such a coating is K = 1.75, which is 1.3 times higher than the similar indicators of the orig-843 inal epoxy matrix. It is shown that the mechanism of material wear is caused by physical 844 and mechanical processes on the surface of composites, the determining factors of which 845 are the processes of microcutting and plastic deformation of the surface layer. Using opti-846 cal and electron microscopy, it is confirmed that branched relief bands are observed on 847 the surface of such a composite, which arose as a result of the action of hydroabrasive 848 particles. At the same time, compared to other studied materials, they are not so deep, and 849 their length is significantly shorter. The improvement in the wear resistance of epoxy com-850 posites can be explained by their improved cohesive properties compared to the epoxy 851 matrix, which implies an increase in the wear resistance coefficient. 852

5. Prospects for future research

Based on the above, it is necessary to state the feasibility of developing new polymer 854 composites, which would be characterized by increased operational characteristics in the 855 complex. To improve the properties of polymers, including those based on epoxy, it is 856 advisable to introduce modifiers into the oligomer, since such additives with a small con-857 tent (1.....3%) allow significantly increasing the functional properties of composites. At the 858 same time, it is important to choose a modifier that contains hydroxyl, carbonyl, nitrile 859 and other groups that are active for physical and chemical interaction with the epoxy oli-860 gomer. It is important to establish the critical content of the additive in the polymer, since 861 its excessive amount leads to an increase in the sol fraction in the materials, which leads 862 to the deterioration of their cohesive strength. 863

Taking into account that the developed materials can be effectively used to protect 864 equipment that is operated under variable loads and at elevated temperatures, it is con-865 sidered appropriate to conduct a study on determining the effect of the nature and content 866 of the modifier on the properties of the epoxy matrix. In addition, it is necessary to state 867 the feasibility of developing new polymer composite materials, which would be charac-868 terized by improved adhesive, physical-mechanical, and thermophysical properties. This 869 is achieved by introducing a modifier and dispersed fillers of various natures. This ap-870 proach, will allow obtaining protective coatings, which are appropriate and necessary to 871 use when restoring parts of machines and mechanisms of transport means. 872

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