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Preparation of Polymer Coatings for Protection of Metal Structures from Corrosive Effects

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Abstract. Copolymers and the methodology for their synthesis are presented. In order to protect metal products and structures from the effects of corrosion processes, various fillers for polymer coating were selected: silicon production waste (microsilica) and titanium dioxide, as well as their combined mixtures. The obtained copolymers exhibit good adhesion required for composite protective coatings. An experiment was conducted to evaluate the corrosion resistance of metals subjected to aggressive environment, as well as to determine the hardness and thickness of the obtained polymer coatings. Thus, the corrosion score of the polymer coating with titanium dioxide filler is 2 in 5% NaCl and 5% KOH aggressive media and is 3–4 in acidic media with 10% KOH. Polymer coating with microsilica filler has a corrosion score of 2 in salt and acid aggressive media, but in alkaline media such coating performed worse and has a corrosion score of 4. The best corrosion resistance values are for the series 2 combination polymer coating consisting of methyl methacrylate, styrene and vinyl butyl ether, with a corrosion score of 2 in salt and acid media and a corrosion score of 4 in alkaline media. Series 1, methyl methacrylate, maleic anhydride, and vinyl butyl ether combined coating has the worst corrosion resistance: corrosion score of 4, 5, 6 in 10% H_2SO_4 and in an alkaline media (5 and 10% KOH), respectively. At the same time, the developed polymer coatings exhibit satisfactory adhesion properties even after the exposure to aggressive media.

Keywords: copolymer synthesis, copolymer, polymer, polymer coating, protective coating, filler, microsilica, titanium dioxide, adhesion

Conflicts of interest. The authors declare that there is no conflict of interest.

Authors' contribution. *Merkulov V.V.* — supervision, project administration, conceptualization; *Volokitina I.E.* — methodology, text writing, reviewing and editing; *Uleva G.A.* — supervision, research; *Epaneshnikova A.E.* — data processing, preparation of initial project.

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Подготовка полимерных покрытий для защиты металлических конструкций от коррозионного воздействия

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Аннотация. Представлены сополимеры и разработана методика их синтеза. Для полимерного покрытия были выбраны различные наполнители — отходы производства кремния (микрокремнезем) и диоксид титана, а также их комбинированные смеси с целью защиты металлических изделий и конструкций от воздействия коррозионных процессов. Полученные сополимеры обладают хорошей адгезией, необходимой для создания композитных защитных покрытий. Проведен эксперимент по определению коррозионной стойкости металлов под воздействием агрессивных сред, а также по определению твердости и толщины полученных полимерных покрытий. Таким образом, коэффициент коррозии полимерного покрытия с наполнителем из диоксида титана составляет 2 в агрессивных средах с содержанием 5 % NaCl и 5 % KOH и 3–4 в кислых средах с содержанием 10 % KOH. Полимерное покрытие с микрокремнеземным наполнителем имеет показатель коррозии 2 в солевых и кислотных агрессивных средах, но в щелочных средах такое покрытие работает хуже и имеет показатель коррозии 4. Наилучшие показатели коррозионной стойкости имеют комбинированные полимерные покрытия серии 2, состоящие из метилметакрилата, стирола и винилбутилового эфира, с показателем коррозии 2 в соленой и кислой средах и 4 в щелочной среде. Комбинированное покрытие серии 1, состоящее из метилметакрилата, малеинового ангидрида и винилбутилового эфира, обладает наихудшей коррозионной стойкостью: показатель коррозии составляет 4, 5, 6 10 % H_2SO_4 и щелочной среде (5 и 10 % KOH) соответственно. В то же время разработанные полимерные покрытия обладают удовлетворительными адгезионными свойствами даже после воздействия агрессивных сред.

Ключевые слова: синтез сополимера, сополимер, полимер, полимерное покрытие, защитное покрытие, наполнитель, микрокремнезем, диоксид титана, адгезия

Заявление о конфликте интересов. Авторы заявляют об отсутствии конфликта интересов.

Вклад авторов. *Меркулов В.В.* — руководство, администрирование проекта, концептуализация; *Волокитина И.Е.* — методология, написание, рецензирование и редактирование; *Ульева Г.А.* — руководство, исследование; *Епанешникова А.Е.* — обработка данных, подготовка первоначального проекта.

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1. Introduction

Concrete and reinforced concrete are the most common building materials, and therefore the problem of increasing the durability of various buildings and structures is particularly relevant. Corrosion protection is one of the most important scientific, environmental, social and economic challenges, since technical progress in many industries is hampered by a number of unresolved problems of corrosion control.

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The significance of corrosion processes is particularly evident in enterprises that use metal structures, equipment, machinery, tools and transportation with substantial wear and tear during their service life. According to open sources, annual direct global losses from corrosion are estimated at 1.8 trillion dollars.[3]

The importance of corrosion studies is determined by three aspects:

- economic — aims to reduce material losses as a result of corrosion of metallic and non-metallic structures and products;
- improving the equipment reliability, which as a result of corrosion can be destroyed with catastrophic consequences;
- metal stock preservation. The world's metal resources are limited, and metal losses due to corrosion lead to additional energy and water costs. Equally important, the human labor spent on the design and reconstruction of metal structures and equipment affected by corrosion can be directed to other socially useful tasks [1; 2].

This is most relevant in countries with a large metal stock due to the increasing use in the industry (construction, metallurgical, machine-building, etc.) not only of high-strength materials, but also of particularly aggressive media, high temperatures and pressures. Under these conditions, the specific weight of metal losses increased significantly.

Polymer coatings are widely used to protect metals from corrosion. They not only protect the metal from corrosive and other chemical influences, but also give the building structure or metal product excellent electrical insulation, decorative, antiseptic and other properties. Compared to paint and enamel, polymer coatings have a number of advantages. They are more durable, more elastic, better bonded to the metal; in the process of operation, they rub off and crack much less than enamels.

The requirements for polymer coatings are quite serious. First, they must exhibit very high surface adhesion as they bond to the metal base at the molecular level rather than just coating it. Polymer coatings not only protect metals from the effects of aggressive environments, but also increase their wear resistance, reducing the adhesion of various substances to the working surfaces, allow saving non-ferrous metals and other scarce materials [3; 4].

Scientists of many countries are engaged in the problem of corrosion of metal building structures or products, developing polymer coatings with the required complex of properties. Thus, in paper [5] the authors cite the technology of obtaining a composition for protective and decorative coating on a building material, including film-forming component (polyester resin 5.0–20.0% wt.), binding component (polyvinyl acetate emulsion 30.0–60.0% wt.), pigment 5.0–30.0% wt., plasticizer (diethylene glycol 2.0–15.0% wt. and butadiene-styrene copolymer in the form of "Bustilat" glue 5.0–10.0% wt.), polymerization initiator (ammonium persulfate 5.0–15.0% wt.) and water (rest). However, this protective coating is a complex composition including expensive functional additives.

The technology of obtaining the composition for the protection of steel structures and equipment made of carbon steel was developed by the authors of [6]: the obtained anticorrosive polymer coating consists of (part weight h): epoxy-diane resin (100), dibutyl phthalate, (10–20), highly dispersed silicon dioxide (1.5–3) with a specific surface area of 150–400 m^2/g, acid hardener (30–50), mineral filler (100–550), accelerant, for example, dimethylaniline (0.1–0.5). Phthalic and maleic anhydrides can be used as acid hardener. The composition ensures increased corrosion and wear resistance. The developed protective polymer coating is difficult to prepare, is multi-component and belongs to hot curing coatings, which limits its application.

In papers [7; 8], a composition for anticorrosion coating used in various industrial fields is proposed, including film-forming agent — copolymer of trifluorochloroethylene with vinylidene fluoride F-32L, organic solvent — acetone, butyl acetate, additionally contains pigments — aluminum powder, or titanium dioxide, and/or blue phthalocyanine pigment, and/or yellow iron oxide pigment, and/or red iron oxide pigment, and/or technical carbon, and as an organic solvent additionally contains toluene and ethyl acetate.

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[3] Corrosion is one of the main problems in the operation of metal structures (In Russ.). 2015. Available from: https://1cert.ru/stati/korroziya-odna-iz-osnovnykh-problem-pri-ekspluatatsii-metallicheskikh-konstruktsiy (accessed: 12.04.2023).

Combination of components in a certain ratio results in coatings with adhesion to steel of 75–810 N/m, impact strength of 12–15 J and drying time of 2.0–2.5 h, while maintaining the values of flexural strength and resistance to vapors of 30% HCl at 90 °C. However, the coating developed by this technology has low adhesion and negligible water resistance.

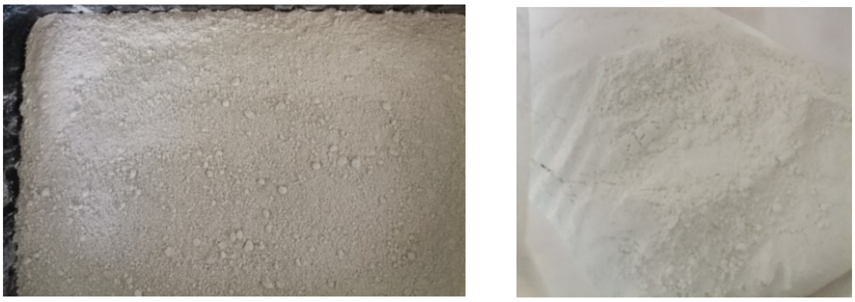
The authors of papers [9; 10] offer a technology for obtaining protective polymer coatings characterized by a composition based on copolymers, solvent, modifier, filler and hardener containing copolymers of vinyl-n-butyl ether (VBE), methyl methacrylate (MMA), maleic anhydride (MA) and low molecular weight dimethyldihexylbutyndiol as a modifier at the following ratio of components, % pts. wt.: copolymer VBE:MMA:MA 30–70, solvent 10–50, modifier 0.5–1.5, filler 20–60, and having corrosion properties of corrosion-resistant coatings.

A lot of scientific studies are aimed at obtaining composite protective polymer coating using silicon production wastes — microsilica (microsilicas, nanosilicas), as well as with zinc production wastes — zinc ashes [11–19].

The filler for polymer coatings is selected depending on the application. For example, for polymer coating of concrete floors, the composition may include silica sand, corundum and other substances that increase strength and resistance to abrasion. For metal surfaces it is steel, aluminum and other powder, as well as fibers. Products with such fillers are close in strength to the base material. The compositions may also include coloring agents [20].

Therefore, effective measures that can lead to the development of polymer protective coatings of new formulations are needed.

The authors of this article, having made a literature and patent analysis, offer a technology for creating a corrosion-resistant polymer coating, using various fillers (Figure 1).



a *b*

Figure 1. Filler appearance: *a* — microsilica; *b* — titanium oxides
Source: made by I. Volokitina

The purpose of this study is to develop a technology for obtaining a composition of protective coating based on copolymers with corrosion properties, as well as the possibility of using this coating to protect against the effects of aggressive environments of metal products.

The object of research is the obtained protective polymer coating with the use of various fillers.

The following tasks are set for fulfillment of the specified purpose:

1) development of the technology of copolymer production;

2) selection of formulation for a new polymer coating for protection of metal structures and products from the effect of aggressive media;

3) selection of fillers for making the polymer coating;

4) development of complex technology of obtaining protective polymer coating on the basis of copolymers;

5) determination of physical and mechanical properties of the obtained corrosion-resistant polymer coating.

In the course of the study, a copolymer based on vinyl butyl ether, styrene and methyl methacrylate was obtained. On the basis of the obtained copolymer, the composition of the protective coating was developed.

2. Methods

Methyl methacrylate and vinyl butyl ether were poured into a three-neck flask and maleic anhydride (copolymer 1) was loaded into the flask. 100 g of toluene was loaded after the maleic anhydride was dissolved. The heating temperature of the monomer mixture is about 60 °C. Then 0.2 g of dinitrilazoisobutyric acid polymerization initiator was added. Copolymerization occurs when slowly heated to a temperature of 70–80 °C for 1–2 hours. The reaction mixture was incubated for 24 hours (1 day) to mature the copolymer.

The synthesis of copolymer 2 (methyl methacrylate and vinyl butyl ether) with different ratios of initial components was carried out in a similar manner. The obtained copolymers were blended with fillers in order to change their technological and operational properties in a directed manner.

After preparation of copolymers (Figure 2–4) of different compositions, they were mixed with fillers — microsilica, titanium oxide and jointly titanium oxide and microsilica at the same copolymer to filler ratio of 3:1. During the mixing of the components, a solvation process occurred with vigorous bubbling lasting 15 min followed by a settling process. The drying time is 24 h after applying polymer coatings to the samples.

Figure 2. Copolymer preparation
Source: photo by I. Volokitina

Figure 3. Finished copolymer materials for coating application
Source: photo by I. Volokitina

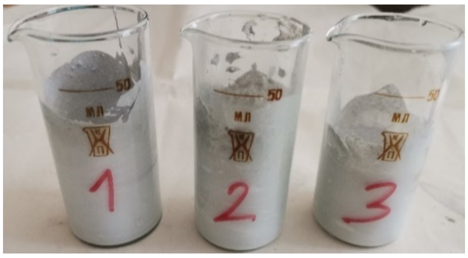


Figure 4. Finished polymer coatings for metal samples
Source: photo by I. Volokitina

Table 1 shows the formulation of the developed protective polymer coatings.

The method used was dip coating, a process in which a substrate is immersed in a liquid and then extracted under controlled environmental conditions, ultimately resulting in a coating.

Determination of hardness, adhesion, thickness of coatings was carried out according to state-approved methods. The microstructure was studied by electron microscopy on a Jeol microscope.

Table 1

Compositions of developed polymer coatings

No. of coverage	Composition			
	Polymers		Filling materials	
	Copolymer 1 MMA:VBE:MA	Copolymer 2 MMA:VBE	SiO_2	TiO_2
1	–	+	–	+
2	–	+	+	–
3	–	+	+	+
4	+	–	–	+
5	+	–	+	–
6	+	–	+	+

Note: MMA — methyl methacrylate; VBE — vinyl butyl ether;
MA — maleic anhydride; SiO_2 — microsilica powder; TiO_2 — titanium dioxide powder.
Source: made by I. Volokitina

3. Results and Discussion

The obtained polymer coatings were applied to metal plates (Figures 5–7).

Figure 5. Polymer coating with titanium oxide filler
Source: photo by A. Yepaneshnikova

Figure 6. Polymer coating with microsilica filler
Source: photo by A. Yepaneshnikova

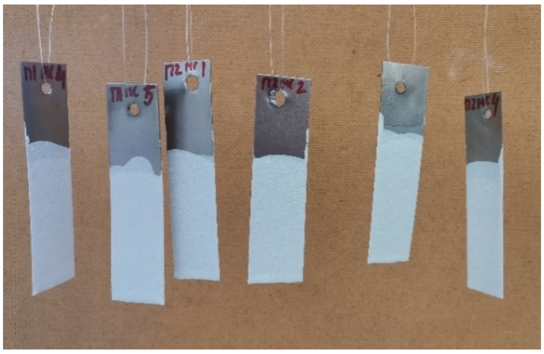
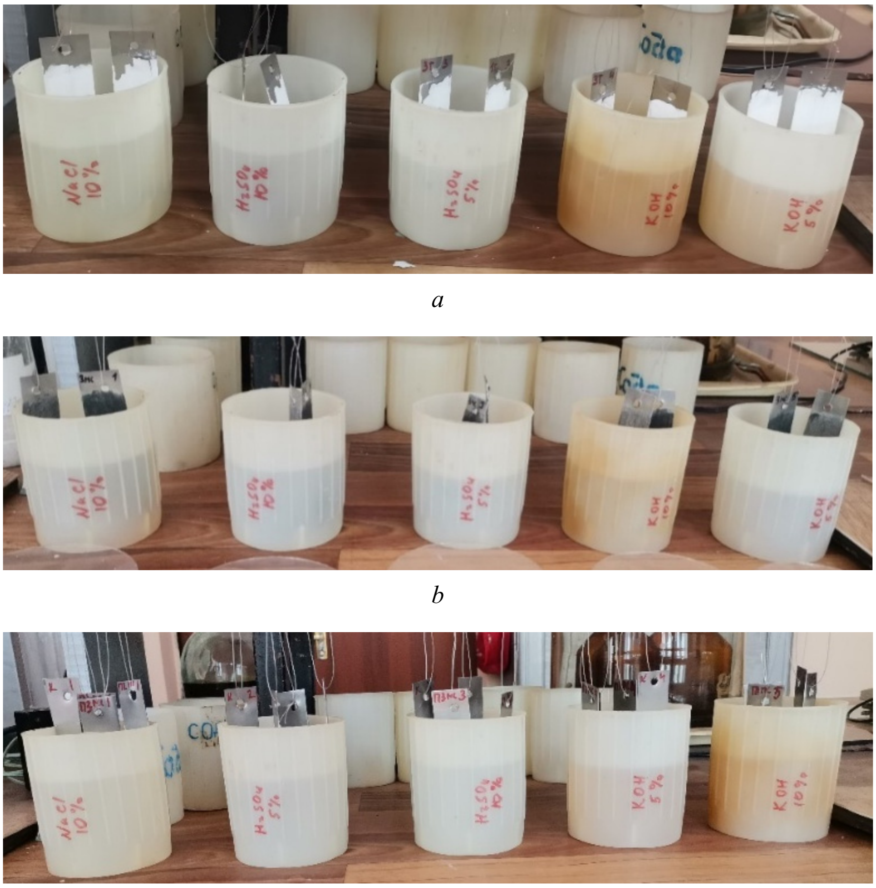


Figure 7. Combined polymer coating
Source: photo by A. Yepaneshnikova

Plates with the studied coating and uncoated plates were placed in different aggressive media in order to determine the behavior of the obtained polymer coatings and to calculate their corrosion resistance. The composition of aggressive media is as follows: H_2SO_4 acid — 5% and 10%; KOH base — 5% and 10%; NaCl salt — 10%. The plates were incubated in aggressive media for 24 hours (Figure 8).



a

b

c

Figure 8. Immersion of metal samples in aggressive media:
a — samples with titanium filler; *b* — samples with microsilica filler; *c* — samples with combined polymer coating
Source: photo by A. Yepaneshnikova

Table 2 describes the behavior of polymer coatings in contact with aggressive media.

According to the results of Table 2, it can be seen that the samples with titanium dioxide filler withstood the test in hydrochloric medium and in 10% KOH medium. Microsilica filled coating showed the best results after exposure to aggressive environments (5% H_2SO_4). Samples with combined polymer coating showed very good results when exposed to aggressive media: salt solution and sulfuric acid solutions.

The appearance of samples after exposure to aggressive media is shown in Figure 9.

The rate of corrosion of metals at their uniform destruction is determined by the depth index K_g (mm/year):

$$K_g = \frac{K_m^- \cdot 8760}{\rho \cdot 1000}, \tag{1}$$

where K_m^- — corrosion rate, *g/(m*^{2}*·h)*; 8760 — number of hours per year; ρ — density of metal, kg/cm^3.

Mass loss per unit surface area Δm, kg/m^2, is calculated by the formula:

$$\Delta_m = \frac{m_0 - m_1}{S}, \tag{2}$$

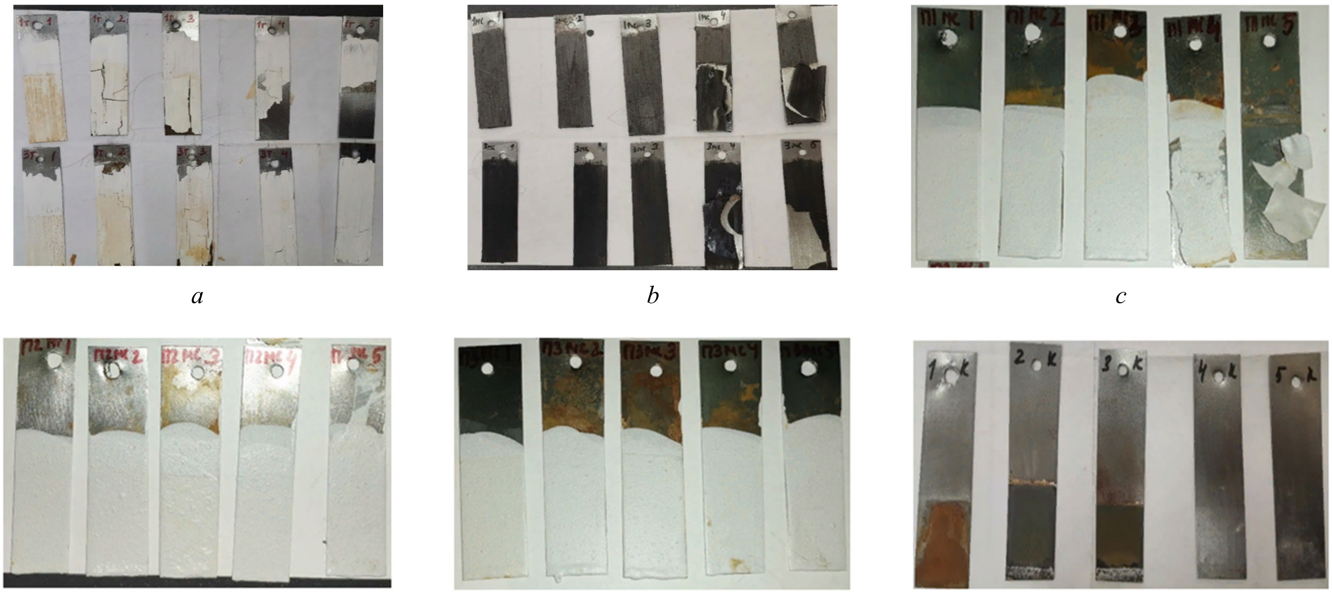
where m_0 — mass of the specimen before testing, kg; m_1 — mass of the sample after testing and removal of corrosion products, kg; S — surface area of the sample, m^2.

Table 2

Description of polymer coating behavior after exposure to aggressive media

NaCl	**H_2SO_4 5%**	**H_2SO_4 10%**	**KOH 5%**	**KOH 10%**
1	2	3	4	5
MMA+VBE+MA+TiO_2 ($1TiO_2$)				
Visually, the coating has not lost its integrity, i.e. it has withstood the effects of the aggressive environment. Corrosion products were isolated on the subcoating	Coating cracked on both sides, integrity damaged. Surface cracks are large and deep. In some areas the coating has peeled off. Corrosion products have also separated under the coating	The coating has peeled off completely on one side. Corrosion products are observed underneath the coating. There are also cracks on the surface of the coating	The coating on 2 sides is completely peeled off (loose from the backing), but there are no traces of corrosion products	The coating has peeled off on 2 sides. There are corrosion products under the coating in some areas
VBE+MMA+TiO_2 ($3TiO_2$)				
The integrity of the coating is intact. Corrosion products have been released under the coating. Small, fine microcracks are observed on the coating	In some areas the coating has peeled off, but less than on the sample of series 1–2 ($1TiO_2$ sample No. 2), there are lso corrosion products under the coating	The coating has bulged and, after drying, has almost completely peeled off on one side. There are corrosion products in a dense layer	After exposure to the aggressive media, the weight of the sample increased, i.e. the coating swelled up. The coating has peeled off, but less than sample No. 4 of series 1. There are no traces of corrosion products under the coating. The coating has a white tint	After exposure to the aggressive media, the weight of the sample increased, i.e. the coating swelled up. The coating has peeled off, but less than sample No. 5 of series 1 and sample No. 4 of series 3. There are no traces of corrosion under the coating. The coating has a white tint
MMA+VBE+MA+SiO_2 ($1SiO_2$)				
The coating has started to peel at the bottom. The coating itself is rough. There are localized corrosion products under the coating	The coating is rough. The surface has cracked, but the coating has not peeled off, it is tightly adhered to the base. There are no corrosion traces	The coating has peeled off from the base on one side, on the other side the coating is tightly adhered to the base. Roughness is observed	The coating has swollen and peeled off on both sides. The coating is rough	The coating has swollen and peeled off on both sides. The coating is rough
VBE+MMA+SiO_2 ($3SiO_2$)				
The coating has preserved its integrity, is tightly adhered, has a uniform structure, and is rough. There are no traces of corrosion under the coating	Although the sample increased in weight after exposure to the aggressive media, the coating itself remained dense and kept its integrity. There are no traces of corrosion under the coating	The coating has preserved its integrity, is tightly adhered, has a uniform structure, and is rough. There are no traces of corrosion under the coating	The coating has swollen and peeled off completely. Corrosion products are observed locally	The coating has swollen and peeled off completely. Corrosion products are observed locally
MMA+VBE+MA+TiO_2+SiO_2 (series 1 combined coating)				
The coating has preserved its integrity, is tightly adhered, has a smooth structure, and is rough. There are no traces of corrosion under the coating	The coating has maintained its integrity, adhering tightly to the base, but is beginning to peel off along the edges of the sample. The coating has a uniform rough structure. There are traces of corrosion under the coating	The coating has preserved its integrity, is tightly adhered, and has a uniform rough structure. There are localized corrosion products under the coating	The coating is swollen and cracked after drying, but there are no corrosion products under the coating	The coating has completely peeled off on both sides; there are also no corrosion products under the coating
MMA+VBE+styrene+SiO_2+TiO_2 (series 2 combined coating)				
The coating has kept its integrity, is tight, has a smooth structure, is rough. But under the coating there are traces of corrosion	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. There are no traces of corrosion under the coating	The coating has maintained its integrity, tightly adhered, has a uniform structure, rough, but locally slightly swollen; there are corrosion products under the coating	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. There are no traces of corrosion under the coating	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. Localized signs of corrosion are beginning to appear
VBE+MMA+SiO_2+TiO_2 (series 3 combined coating)				
The coating has kept its integrity, is tightly adhered, has a smooth structure, is rough, but under the coating there are corrosion products in a continuous layer	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. No traces of corrosion are under the coating	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. There is delamination of the coating on the edges. But under the coating there are local traces of corrosion	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. There are no corrosion traces under the coating	The coating has maintained its integrity, is tightly adhered, has a uniform structure, and is rough. There are no corrosion traces under the coating
Check sample (uncoated)				
The sample is fully corroded on both sides	Corrosion products are observed on the surface, but corrosion of the sample metal itself has not occurred	Both corrosion products and salt residues are observed on the surface. Corrosion products lie on the metal surface in a dense layer on both sides	There are no traces of corrosion, only roughness appeared in some areas after exposure to aggressive media	There are no traces of corrosion, only roughness appeared in some areas after exposure to aggressive media

Source: made by I. Volokitina



a *b* *c*

d *e* *f*

Figure 9. Appearance of samples after exposure to aggressive media:
a — coating with titanium filler (series 1); *b* — coating with titanium filler (series 2);
c — coating with microsilica filler (series 1); *d* — coating with microsilica filler (series 2);
e — combined polymer coating (series 1, series 2, series 3); *f* — metal samples without coating
Source: photo by A. Yepaneshnikova

Table 3 shows the weight of coated samples before and after exposure to aggressive media and corrosion score according to Interstate standard GOST 9.908–85[2].

Table 3

Results of determination of corrosion weight score of polymer coatings with fillers (microsilica and titanium oxide)

Parameter	**Coating 1TiO₂**	**Coating 3TiO₂**	**Coating 1SiO₂**	**Coating 3SiO₂**
5% NaCl				
m_0, g	12.43	11.92	11.78	12.19
$m_{к}$, g	12.45	11.88	11.81	12.16
V, g/m^2*h	0.00083	0.00167	0.00125	0.00125
C_m^-	0.001	0.0019	0.0014	0.0014
R, %	quite resistant / 2	quite resistant / 2	quite resistant / 2	quite resistant / 2
Δm, %	0.16	0.34	0.25	0.25
5% H_2SO_4				
m_0, g	11.94	11.60	11.11	11.56
$m_{к}$, g	11.56	11.24	11.14	11.60
V, g/m^2*h	0.0158	0.0150	0.00125	0.00167
C_m^-	0.0178	0.0169	0.0014	0.0019
R, %	resistant / 4	resistant / 4	quite resistant / 2	quite resistant / 2
Δm, %	3.18	3.10	0.27	0.35

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[2] GOST 9.908–85. Unified system of corrosion and ageing protection. Metals and alloys. Methods for determination of corrosion and corrosion resistance indices. 1989. (In Russ.)

Ending of the Table 3

Parameter	**Coating 1TiO$_2$**	**Coating 3TiO$_2$**	**Coating 1SiO$_2$**	**Coating 3SiO$_2$**
10% H$_2$SO$_4$				
m_o, g	11.90	11.86	13.02	15.76
$m_к$, g	11.72	11.68	13.06	15.73
V, g/m^2*h	0.0750	0.0750	0.00167	0.00125
C_m^-	0.0084	0.0084	0.0019	0.0014
R, %	quite resistant / 3	quite resistant / 3	quite resistant / 2	quite resistant / 2
Δm, %	1.51	1.52	0.31	0.19
5% KOH				
m_o, g	11.33	11.45	11.89	12.14
$m_к$, g	11.42	11.49	12.30	11.10
V, g/m^2*h	0.0038	0.00167	0.01708	0.04333
C_m^-	0.0042	0.0019	0.0192	0.0487
R, %	quite resistant / 2	quite resistant / 2	resistant / 4	resistant / 4
Δm, %	0.79	0.35	3.45	8.57
10% KOH				
m_o, g	12.50	12.15	12.08	16.37
$m_к$, g	12.17	12.63	12.67	15.39
V, g/m^2*h	0.0138	0.0200	0.0246	0.0408
C_m^-	0.0154	0.0225	0.0276	0.0459
R, %	resistant / 4	resistant / 4	resistant / 4	resistant / 4
Δm, %	2.64	3.95	4.88	6.00

Source: made by I. Volokitina

The results of Table 3 show that the introduction of maleic anhydride into the composition of polymer coating significantly increases corrosion processes, i.e. decreases their corrosion resistance. Effect of aggressive media: the series samples with TiO$_2$ filler withstood the effect of aggressive media better in hydrochloric and alkaline solutions, and the series samples with SiO$_2$ filler can perform well, on the contrary, in acidic media.

Table 4 shows the weight of samples with combined polymer coating before and after exposure to aggressive media and the corrosion score.

The results of Table 4 show that the combined polymer coating of series 2 performed well in hydrochloric and acidic solutions, worse in alkaline solutions. This is probably due to the presence of styrene in the composition of the combined coating, which has good resistance to aggressive media. Series 1 combined polymer coating has good resistance to salt solution and 5% H$_2$SO$_4$ solution. Series 3 combined polymer coating has average values of corrosion resistance in all presented aggressive media (score not higher than 4). The combined polymer coating with microsilica filler performed the worst in aggressive media; it has the highest corrosion rate, weight loss and corrosion scores.

Figure 10 shows a comparative plot of the change in corrosion rate of polymer coatings after exposure to aggressive media.

Figure 11 shows a comparative analysis of the weight change of the polymer coatings after exposure to aggressive media, and Figure 12 shows the score of the polymer coatings.

Figures 10–12 show that the combined polymer coating with microsilica filler performed the worst in aggressive media; it has the highest corrosion rate, mass loss and corrosion score.

Table 4

Results of determining the corrosion weight score of the combined polymer coating

Parameter	**1Methyl methacrylate + Maleic anhydride + Vinyl butyl ether +TiO_2 (titanium oxide) + SiO_2 (microsilica) series 1**	**2Methyl methacrylate + Vinyl butyl ether + styrene + TiO_2 (titanium oxide) + SiO_2 (microsilica) series 2**	**3Methyl methacrylate + Vinyl butyl ether + TiO_2 (titanium oxide) + SiO_2 (microsilica) series 3**
5% NaCl			
m_o, g	12.87	12.53	16.78
$m_{к}$, g	12.85	12.47	16.66
V, g/m^2*h	0.0008	0.0250	0.0050
C_m^-	0.001	0.0028	0.0056
R, %	quite resistant / 2	quite resistant / 2	quite resistant /3
Δm, %	0.16	0.48	0.71
5% H_2SO_4			
m_o, g	12.68	12.98	12.52
$m_{к}$, g	12.63	12.95	12.43
V, g/m^2*h	0.0021	0.0013	0.0038
C_m^-	0.0023	0.0014	0.0042
R, %	quite resistant / 2	quite resistant / 2	quite resistant / 2
Δm, %	0.39	0.23	0.72
10% H_2SO_4			
m_o, g	17.11	17.26	16.95
$m_{к}$, g	16.86	17.21	17.09
V, g/m^2*h	0.0104	0.0021	0.0058
C_m^-	0.0117	0.0023	0.0066
R, %	resistant / 4	quite resistant / 2	quite resistant / 3
Δm, %	1.46	0.29	0.83
5% KOH			
m_o, g	11.65	12.42	12.55
$m_{к}$, g	12.87	12.73	12.86
V, g/m^2*h	0.0508	0.0129	0.0129
C_m^-	0.0571	0.0145	0.0145
R, %	resistant / 5	resistant / 4	resistant / 4
Δm, %	10.47	2.50	2.47
10% KOH			
m_o, g	16.53	13.61	12.34
$m_{к}$, g	12.59	13.20	12.59
V, g/m^2*h	0.1642	0.0171	0.0104
C_m^-	0.1844	0.0192	0.0117
R, %	low-resistant / 6	resistant / 4	resistant / 4
Δm, %	23.84	3.01	0.36

Source: made by A. Yepaneshnikova

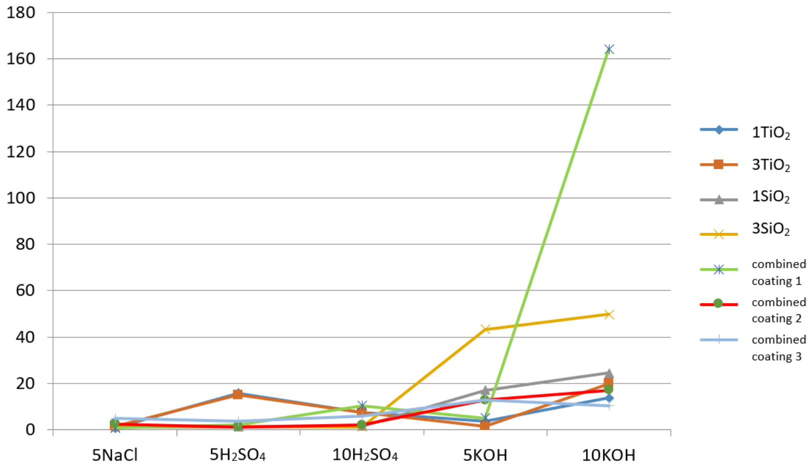

Figure 10. Graph of change in corrosion rate of polymer coatings after exposure to aggressive media
Source: made by G. Ulyeva

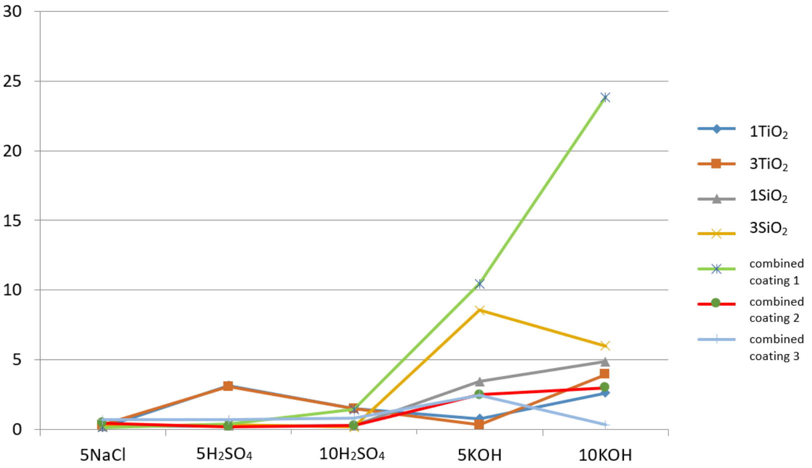

Figure 11. Graph of change in weight of polymer coatings after exposure to aggressive media
Source: made by G. Ulyeva

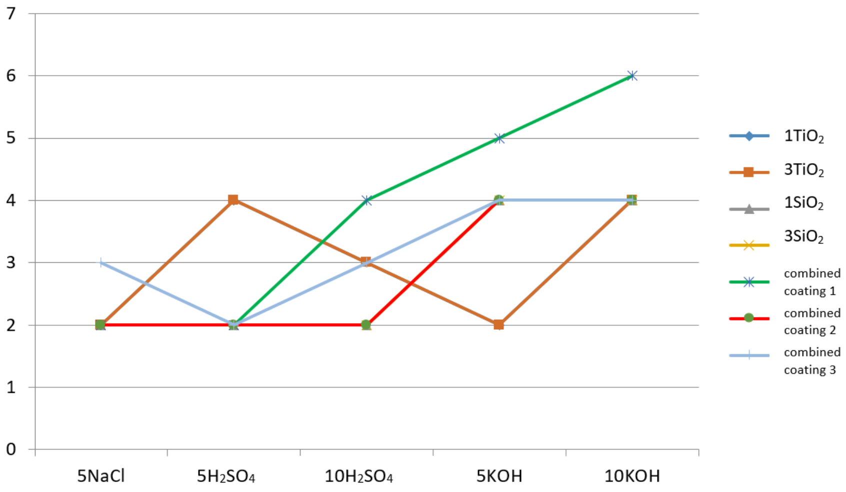

Figure 12. Score of polymer coatings
Source: made by G. Ulyeva

The photo shows microstructures of polymer coatings (Figure 13–19) obtained from the scanning electron microscope “Zeiss” in laboratory of metal science and defectoscopy of the Analytical Control Center of “Qarmet” JSC.

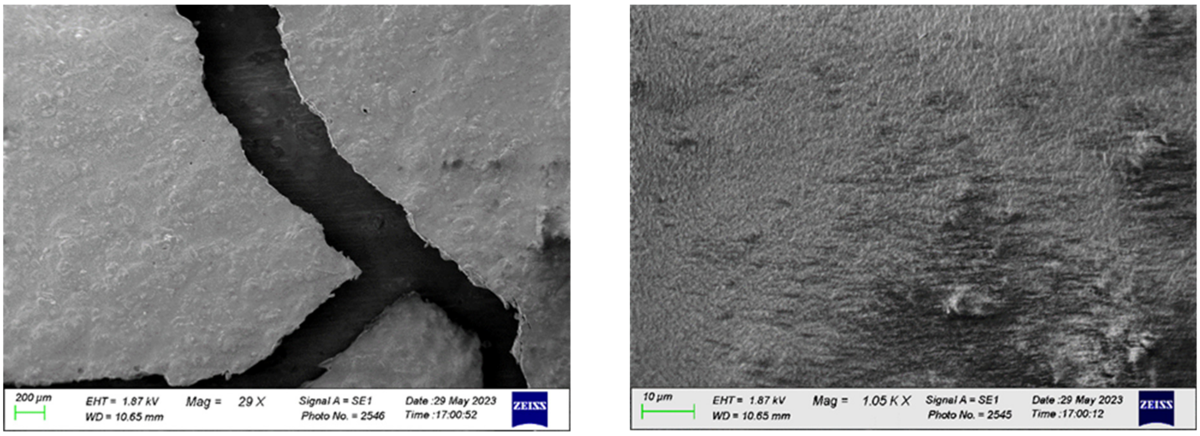

Figure 13. $1SiO_2$ polymer coating after exposure to aggressive media
Source: made by G. Ulyeva

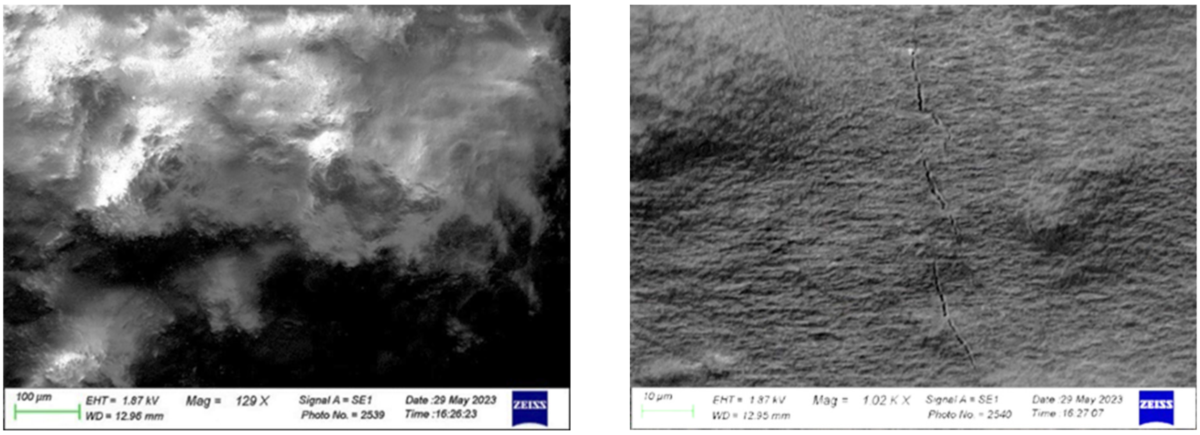

Figure 14. $3SiO_2$ polymer coating after exposure to aggressive media
Source: made by G. Ulyeva

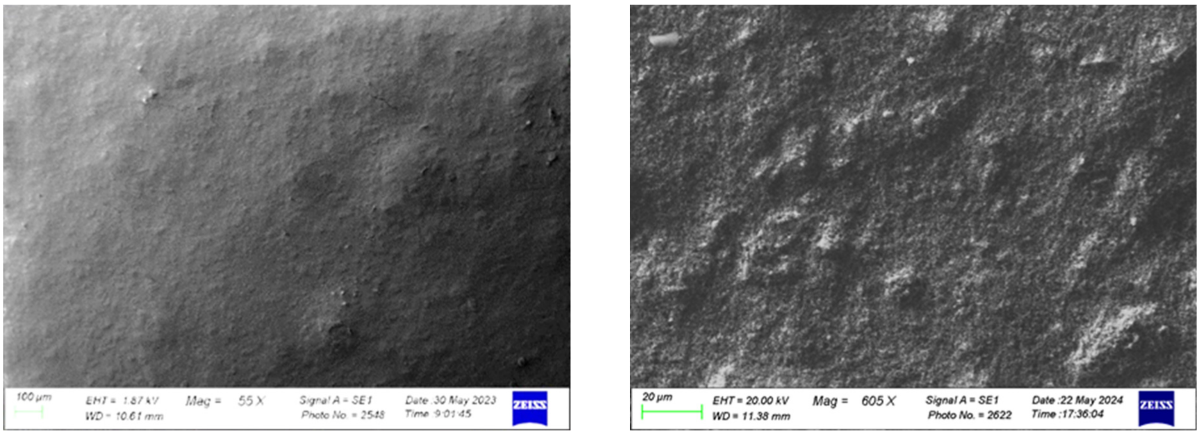

Figure 15. $1TiO_2$ polymer coating after exposure to aggressive media
Source: made by G. Ulyeva

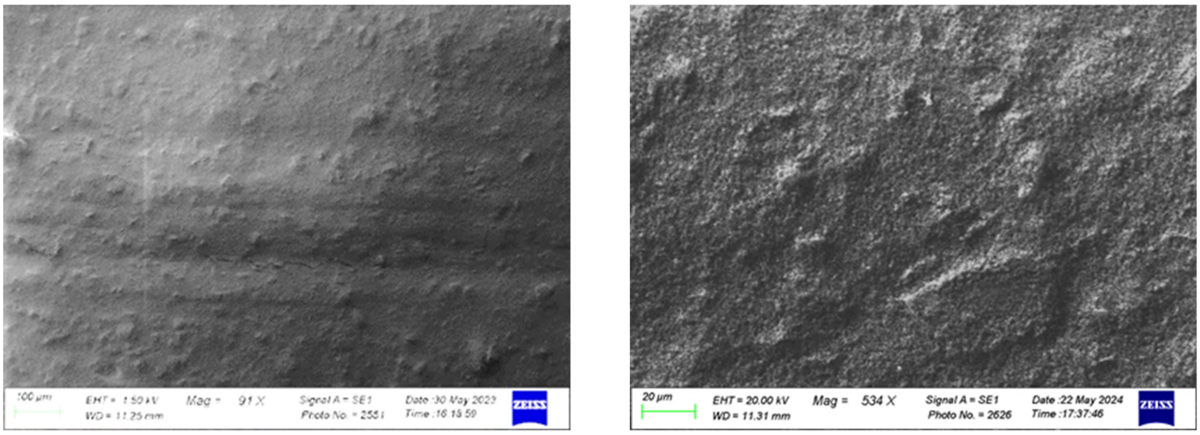

Figure 16. $3TiO_2$ polymer coating after exposure to aggressive media
Source: made by G. Ulyeva

Figure 13 shows that the $1SiO_2$ polymer coating has a uniform homogeneous structure after exposure to the aggressive media. The $3SiO_2$ polymer coating after exposure to aggressive media is also uniform and homogeneous, but local microcracks are observed at high magnification (Figure 14). $1TiO_2$ polymer coating has a similar structure after exposure to aggressive media (Figure 15). In polymer coating $3TiO_2$ after exposure to aggressive media microcracks are observed in some places already at low magnification, the coating itself has a uniform homogeneous structure (Figure 16).

Combined polymer coating of series 1 after exposure to aggressive media has a uniform homogeneous structure, microcracks are also observed in some areas at low magnifications (Figure 17).

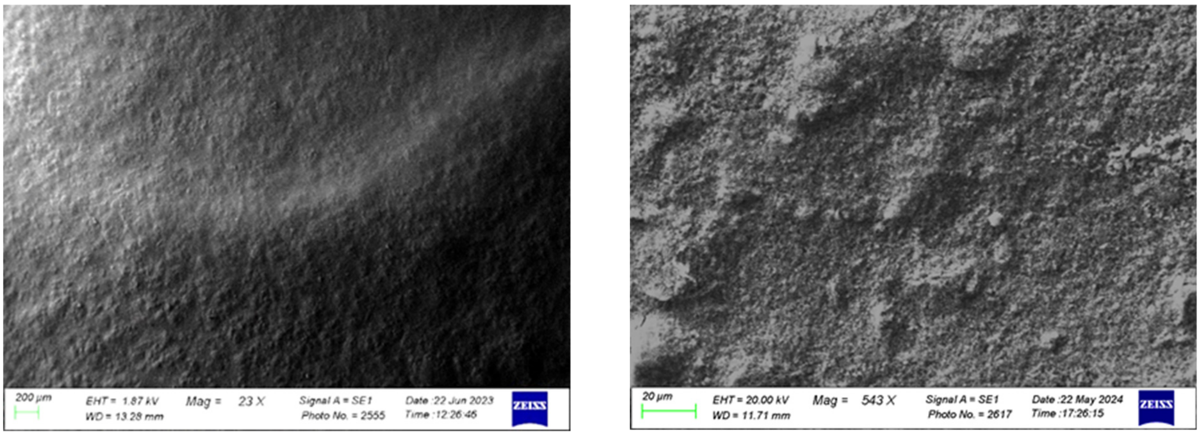

Figure 17. Combined polymer coating of series 1 after exposure to aggressive media
Source: made by G. Ulyeva

Combined polymer coating of series 2 after exposure to aggressive media is characterized by a somewhat heterogeneous structure, there is a local swelling of the coating, but there are no microcracks (Figure 18).

Combined polymer coating of series 3 after exposure to aggressive media is characterized by a uniform, homogeneous structure, there is an interesting pattern of "crystallization", and there are no microcracks (Figure 19).

Further, the adhesion of the polymer coating to the metal base was analyzed by scratch grid method according to Interstate standard GOST 15140–78[3]. The scratch grid method consists in that four-six parallel

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[3] GOST 15140–78. *Paintwork materials. Methods for determination of adhesion*. Standartinform Publ.; 2009. (In Russ.)

lines with depth to the base metal at a distance of 2–3 mm from each other and four-six parallel lines perpendicular to the first ones are drawn on the surface of the controlled coating with a steel point. No peeling should be observed on the controlled surface of the coating[4].

Figure 20 shows the applied scratch grid on the polymer coating.

Table 5 shows the test results of polymer coatings with different filler for adhesion properties.

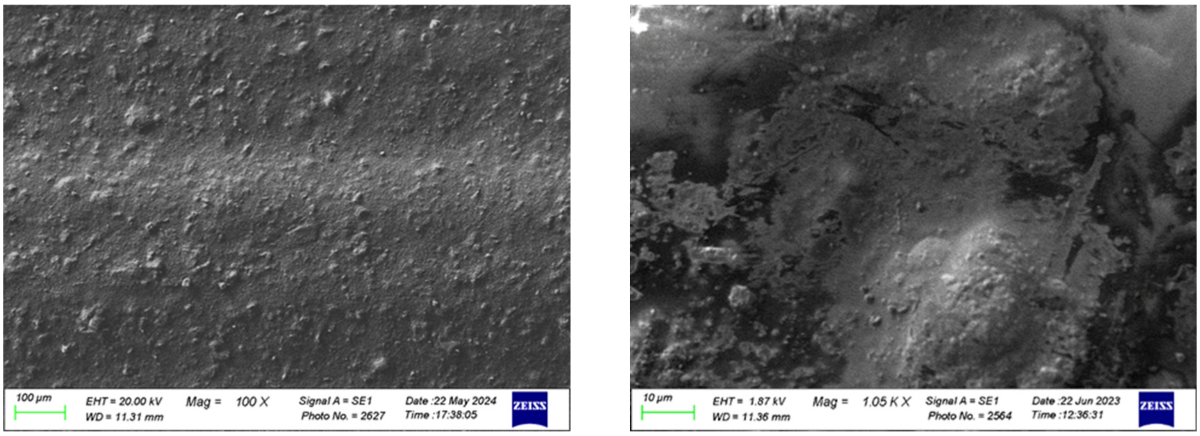

Figure 18. Combined polymer coating of series 2 after exposure to aggressive media
Source: made by G. Ulyeva

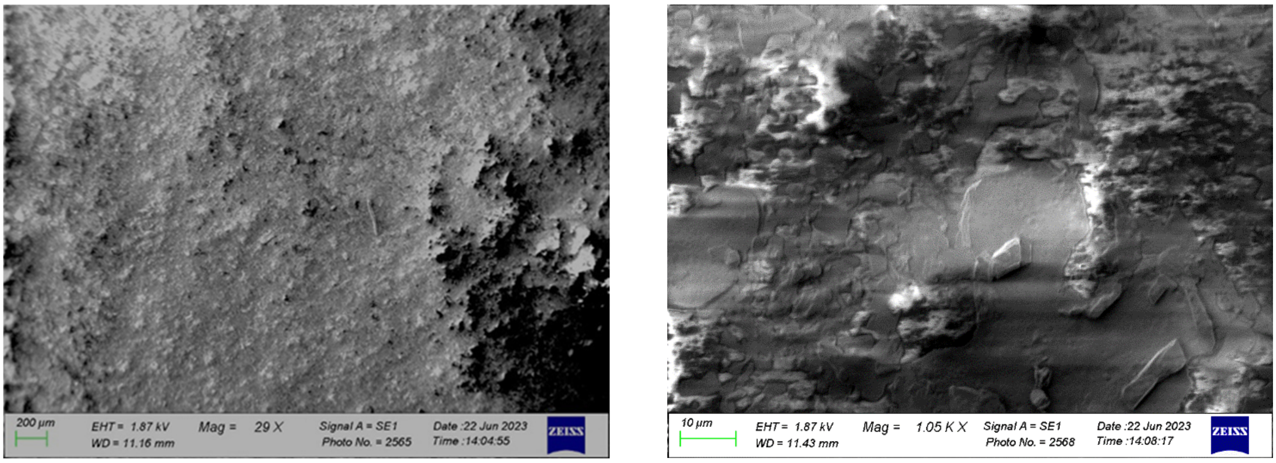

Figure 19. Combined polymer coating of series 3 after exposure to aggressive media
Source: made by G. Ulyeva

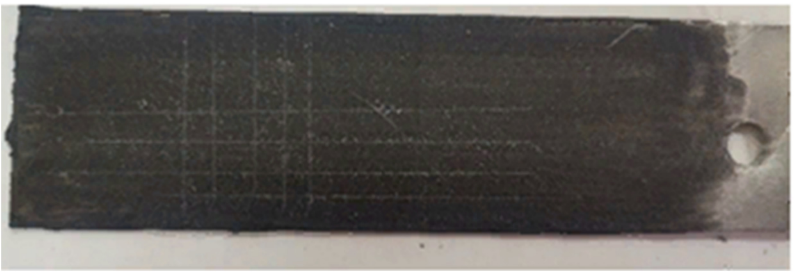

Figure 20. Example of scratch grid application
Source: made by V. Merkulov

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[4] Hardness testers. Available from: http://www.tverdomer.ru/products/portable-hardness-testers (accessed: 25.02.2024).

Table 5

Determination of adhesion of polymer coatings on metal samples

NaCl	H_2SO_4 5%	H_2SO_4 10%	KOH 5%	KOH 10%
1	2	3	4	5
MMA+VBE+MA+TiO_2 (1TiO_2)				
No delamination of the coating during scratch application	The coating crumbled when the scratch grid was applied	The coating crumbled when the scratch grid was applied	The coating crumbled when the scratch grid was applied	The coating crumbled when the scratch grid was applied
VBE+MMA+TiO_2(3TiO_2)				
When applying the scratch grid, the coating peeled off locally (in one place), but overall withstood the test	The coating generally has good adhesion but crumbles at the intersections of the scratch grid	The coating adheres tightly to the base; there is no peeling in all the scratch grid crosshairs	The coating has completely peeled off when the scratch grid was applied	The coating has completely peeled off when the scratch grid was applied
MMA+VBE+MA+SiO_2 (1SiO_2)				
The coating did not peel off when the scratch grid was applied	The coating did not peel off when the scratch grid was applied	The coating has completely peeled off when the scratch grid was applied	The coating has completely peeled off when the scratch grid was applied	The coating has completely peeled off when the scratch grid was applied
VBE+MMA+SiO_2 (3SiO_2)				
When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	The coating has completely peeled off when the scratch grid was applied	The coating has completely peeled off when the scratch grid was applied
MMA+VBE+MA+TiO_2+SiO_2 (1 series combined)				
When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When the scratch grid was applied, the coating did not peel off, leaving scratches in the coating but still adhering tightly to the base	The coating has completely peeled off after exposure to aggressive media	The coating has completely peeled off after exposure to aggressive media
MMA+VBE+styrene+TiO_2+SiO_2 (2 series combined)				
When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base
VBE+MMA+SiO_2+TiO_2 (3 series combined)				
When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base	When applying the scratch grid, the coating did not peel off, tightly adheres to the base

Source: made by V. Merkulov

According to the results of Table 5, it can be seen that samples No. 1 of 1TiO_2 and 3TiO_2 series have good adhesion properties with the base. Samples Nos. 1–2 of 1SiO_2 series and samples Nos. 1–3 of 3SiO_2 series have the best adhesion properties with the base. Series 2 and 3 combined polymer coatings have the best adhesion properties.

Series 1 combined polymer coating has good adhesion properties except for the samples exposed to aggressive media (5 and 10% KOH).

The authors decided to determine the hardness of the coatings in order to evaluate the effect of coating composition and aggressive media on this mechanical characteristic. Hardness was determined using a MET-UD portable combination hardness tester. Hardness was determined on a selected Brinell scale. This hardness tester determines hardness electronically by measuring the change in ultrasonic frequency and by determining the ratio of the velocity of the striker inside the transducer before and after impact.

The striker, located in the dynamic sensor, has a carbide ball at the end, which is directly connected to the controlled surface at the moment of impact. There is a permanent magnet inside the striker. After the trigger is pressed, the striker is ejected onto the surface to be measured by means of a preloaded spring. In this case, the striker moves inside the inductance coil and induces EMF in it by its magnetic field. The signal from the output of inductance coil is fed to the input of the electronic unit, where it is converted to the value of hardness of the selected scale and displayed on the screen.

Table 6 shows the average Brinell hardness results of the samples after exposure to aggressive media.

Table 6

Results of hardness measurements of polymer coating samples on metal

Solution	Hardness, HB				
	Coating 1TiO_2	Coating 3TiO_2	Coating 1SiO_2	Coating 3SiO_2	Cncoated sample
5% NaCl	244.6	219.4	210.6	214.8	204.4
5% H_2SO_4	233.2	233.8	182.4	195.4	211.6
10% H_2SO_4	272.2	239.0	247.0	175.4	200.4
5% KOH	310.6	227.0	232.0	264.4	192.0
10% KOH	221.5	228.6	192.6	230.4	203.4
Medium	254.4	229.6	212.9	216.1	202.4

Source: made by G. Ulyeva

According to Table 6, the highest hardness values are found in titanium filled coatings of both series. Accordingly, the uncoated sample has the lowest values, indicating exposure to aggressive media and metal corrosion. It can be concluded that both titanium-filled and microsilica-filled coatings have protective properties against corrosion, since the hardness of the polymer-coated samples is greater than that of the uncoated sample.

Table 7 shows the average hardness results of the combined polymer coating samples after exposure to aggressive media according to the Brinell method.

Table 7

Results of hardness measurements of combined polymer coating samples on metal

Solution	Hardness, HB		
	Series 1 coating	Series 2 coating	Series 3 coating
5% NaCl	133.7	253.7	187.7
5% H_2SO_4	156.7	182.8	239.7
10% H_2SO_4	150.0	143.0	168.8
5% KOH	233.3	206.0	248.0
10% KOH	204.0	233.0	231.3
Medium	175.5	203.7	215.1
Not covered	213.0	214.5	203.5

Source: made by G. Ulyeva

According to Table 7, the hardness of metal samples with combined polymer coating is less than that of polymer coated samples with different fillers individually. However, the combined polymer coating of series 3 has the highest hardness value compared to series 1 and 2.

The thickness of coatings was also determined in accordance with National standard of the Russian Federation GOST R52146-2003[5] "Polymer-coated rolled products". Table 8 shows the results of determining the thickness of the polymer coating using an electronic micrometer MK-25 (mechanical testing laboratory of the Analytical Control Center of "Qarmet" JSC) after exposure to aggressive media.

Table 8

Results of thickness measurements of polymer coatings with titanium oxide and microsilica fillers, μm

Solution	Coating $1TiO_2$	Coating $3TiO_2$	Coating $1SiO_2$	Coating $3SiO_2$
5% NaCl	0.096	0.152	0.217	0.687
5% H_2SO_4	0.093	0.093	0.267	0.197
10% H_2SO_4	0.059	0.103	0.338	0.256
5% KOH	0.875	0.113	0.159	0.179
10% KOH	0.119	0.091	0.220	0.277
Medium	0.249	0.111	0.241	0.320

Source: made by G. Ulyeva

According to the results of Table 8, it can be seen that the highest thickness values have the polymer coating with microsilica filler of series 3, but at the same time this coating has low hardness values. Conversely, the titanium filled polymer coating, especially series 3, having low thickness values, has higher hardness values.

Table 9 shows the results of the combined polymer coating thickness determination.

Table 9

Thickness measurement results of combined polymer coatings, μm

Solution	Series 1	Series 2	Series 3
5% NaCl	0.294	0.389	0.349
5% H_2SO_4	0.300	0.383	0.267
10% H_2SO_4	0.415	0.527	0.409
5% KOH	0.236	0.472	0.379
10% KOH	0.177	0.492	0.313
Medium	0.284	0.453	0.343

Source: made by A. Yepaneshnikova

According to Table 9, the combined polymer coating of series 2 has the maximum thickness values, which also performed well in aggressive media. Series 3 combined polymer coating with poor resistance to aggressive media has average thickness values. The combined polymer coatings of series 2 and 3 had higher thickness, which means that their initial formulation shall be taken into consideration. The combined polymer coating had a low viscosity when it was created, and initially already had a low thickness.

Thus, the technology of protective coatings of a new composition used for metallic and non-metallic products operating in aggressive media was developed. The new formulation of developed polymer protective coatings favorably distinguishes the proposed composition from the existing ones.

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[5] GOST R52146–2003. Cold rolled and cold rolled hot-galvanized sheet with polymer coating, prepainted by the continuous coil-coating process. Moscow: Izdatel'stvo standartov Publ.; 2004.

4. Conclusion

1. The formulation of corrosive polymer coating with various fillers for protection of metal structures and products from the harmful effects of corrosion was developed. The behavior of different polymer coatings in aggressive media (acidic, neutral, and alkaline) with fillers of microsilica, titanium dioxide and their combination were also considered.

2. It was found that the polymer coating with microsilica filler performed well in acidic environments (5 and 10% H_2SO_4), while the polymer coating with titanium dioxide filler performed well in hydrochloric (10% NaCl) and alkaline (5 and 10% KOH) environments.

3. The best performance was achieved by the combined polymer coating series 2, which performed well in hydrochloric and acid solutions, worse in alkaline solutions (corrosion score 2–4). This is due to the presence of styrene in the composition of the combined coating, which has good resistance to aggressive media.

4. The use of production waste as secondary raw materials coming from electrothermal, metallurgical, coke and chemical industries will serve as a basis for the creation of new production in order to strengthen and develop the economy and will reduce the environmental load, as well as reduce the area of storage of production waste.

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