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Machine-building anti-corrosion composite polymeric materials and coatings based on local raw materials and production waste

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Abstract. The article discusses the results of a study on the development of effective compositions of anticorrosive composite polymer materials and coatings filled with organic-mineral ingredients based on epoxy resins ED-16 and ED-20. The compositions of the developed anticorrosive polymer compositions and the main physical-chemical and mechanical properties of the developed anticorrosive compositions based on oligomers and other organic-mineral ingredients are given.

1 Introduction

The main function of the anti-corrosion coating is to protect the coated surface from the occurrence and penetration of chemical, electrochemical and other processes that lead the surface of products to corrosion destruction.

Even the most durable structures are exposed to corrosion, as a result of which production, financial and temporary losses occur. Being in the air or soil, unprotected steel undergoes corrosion, which results in the destruction of the steel microstructure. Therefore, steel structures for protection against corrosion damage are protected with high-strength metal or anti-corrosion polymer coatings so that they can withstand corrosion-mechanical stresses throughout the service life specified by the technical conditions.

Currently, modern complex and expensive technological equipment, operated in the aggressive conditions of oil and gas and metallurgical enterprises, is subject to corrosion. Corrosion destruction of structures, pipes, tanks and other equipment of these enterprises always requires the development of anti-corrosion protection. Effective anti-corrosion protection provides a long period of equipment operation without repair, reduces the cost of metal production, and also saves energy resources [1, 2].

The use of epoxy compositions, as a rule, is associated with the use of modifiers (fillers, plasticizers, etc.) that regulate the structure and properties of materials. The curing of such multicomponent systems is a complex process involving both the formation of a spatially cross-linked polymer matrix and the formation of its structure. The degree of structuring of the polymer system depends not only on the bond strength of the polymer-filler and the specific surface area of the latter, but also on the type, content and ratio of fillers in the composition.

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Sufficiently wide application for anticorrosion protection in the chemical, petrochemical and metallurgical industries has found coatings made of composite polymer and paint materials [3, 4].

Composite polymeric materials intended for use in aggressive environments in the form of a coating, in addition to anticorrosion properties, must also have high adhesive properties to metal surfaces [5, 6].

The work [7] presents the development of anticorrosive chemically resistant polymer coatings for equipment in the chemical and petrochemical industries. It is shown that coatings based on epoxy vinyl ether and epoxy lacquer ether oligomeric matrices with evenly distributed particles of chemically resistant glass in the form of flakes have the widest range of resistance to aggressive media (acids, alkalis, chlorine-containing organic compounds, kerosene, diesel fuel, nitrobenzene, etc.). or fibers, the linear dimensions of which are related as 1:10. Thin plates of iron mica (alpha-Fe_2O_3 with a hematite structure) are also used as fillers. Such particles of chemically resistant fillers create a coating structure with high barrier properties that prevents the penetration of aggressive agents to the protected metal surface.

Polymer materials deposited in the form of thin films on metal surfaces withstand heavy loads, provide better heat removal, and are less susceptible to dimensional changes than cast polymer parts [8, 9].

In recent years, there has been an increased interest in the use of thin-layer polymer coatings of metals and other materials in mechanical engineering, instrument making, chemical, food, electrical industry, in construction and other areas of the national economy. In our country and abroad (USA, England, France, Germany, Japan), about 30-35% of the total amount of polymeric materials produced is used for coatings. This is due to the fact that the coatings provide a successful combination of the properties of metal and polymeric materials. In addition, due to the wide range of the latter and their relatively easy modification, it is possible to impart the necessary specific properties to the metal surface. They also protect chemical devices, machine parts, pipe fittings, steel structures from moisture absorption and mechanical damage from corrosion; increase the antifriction and wear-resistant properties of parts and friction units made of insufficiently wear-resistant materials; eliminate or reduce the adhesion of processed materials to the surface of the equipment, provide electrical insulation, etc. [10-15].

Measures are being taken in the republic to increase the durability of technological equipment at industrial and other enterprises operating in aggressive environments, which are of particular relevance in the current conditions of the development of economic relations [2, 5, 9].

The aim of the study is development of machine-building anticorrosive composite polymer materials and coatings based on local raw materials and industrial waste.

2 Objects and methods of research

The objects of study are epoxy resin - ED-16, ED-20 and fillers talc, titanium oxide, soot, Angren kaolin - AKT-10, graphite, zinc oxide, and also as a hardener - polyethylenepolyamine - PEPA, as a plasticizer - gossypol resin.

To determine the quality of the developed anti-corrosion polymer composite materials and coatings based on the ED-16, ED-20 oligomer and other organic-mineral ingredients, modern methods of physicochemical and mechanical analyzes were used: Fourier (IR) - spectroscopy, X-ray phase analysis, modulus of elasticity in bending, flexural strength, heat resistance according to Vicat, dielectric constant, specific surface electrical resistance and others.

3 Results and their discussion

By introducing certain fillers into epoxy compositions, it is possible to obtain compositions with predetermined properties. The fillers introduced into the binders turn them into heterogeneous systems consisting of the solid phase of the filler (powders, metal particles) and the liquid phase - resin, distributed over the surface of the filler in the form of thin films.

Based on the analysis of theoretical and experimental studies carried out by us, scientifically based principles and the requirement to create effective anticorrosive composite materials based on polymers and organic-mineral ingredients were formulated [1, 2, 6]:

the polymeric materials used must have, first of all, manufacturability, high adhesive strength and chemical resistance;

the absorption of vapors of aggressive media should be within 0.60-0.65 kPa at a pressure of up to 10 kPa in the absence of fillers and 0.50-0.55 kPa in their presence;

the value of the relative diffusion coefficient should be within 30-35%;

the value of the dielectric constant of anti-corrosion compositions should be in the range of 5.0-6.0;

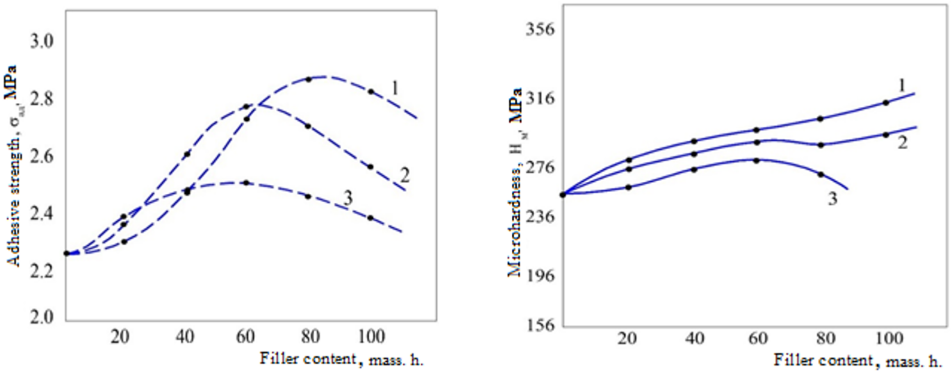
an increase in the service life of anti-corrosion materials should be achieved by their physical modification with fillers containing metal oxides;

should be in the range of 25-35 mass.p.

To develop effective formulations of anticorrosive polymeric composite materials and coatings based on ED-16, ED-20 oligomer and other organic-inorganic ingredients, the effect of organic-mineral fillers on their basic physical-chemical and mechanical properties was studied.

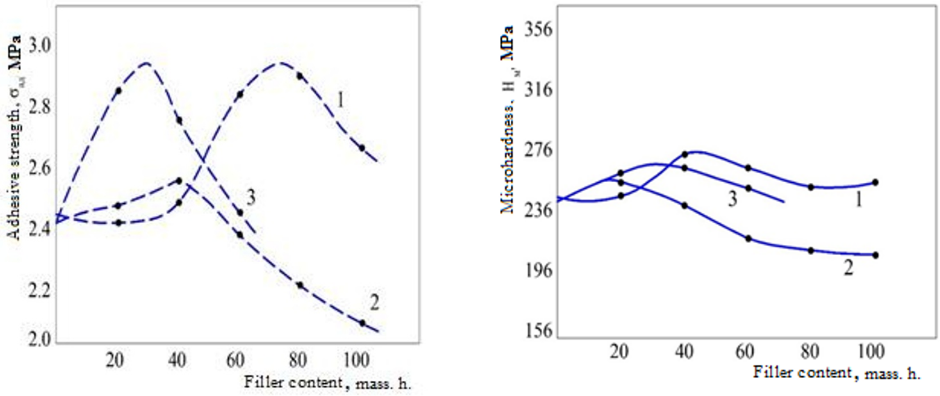
As noted above, the most important strength properties of coatings are their adhesive strength and microhardness. In this regard, we conducted studies to determine the adhesive strength and microhardness of the developed anticorrosion composite epoxy polymeric materials and coatings based on them, filled with various organic-mineral fillers. In this aspect, the influence of selected organic-mineral fillers on the properties of polymers such as kaolin, titanium oxide, graphite, talc, carbon black and zinc oxide, which are representatives of mineral fillers and metal oxides and electrically conductive fillers, was investigated.

Results of studies of the effect of the studied organic-mineral fillers on adhesive strength and microhardness anti-corrosion composite epoxy polymer materials are shown in Figures 1 and 2.



a) *b)*

Fig. 1. Dependence of adhesive strength (a) and microhardness (b) of anticorrosion composite epoxy polymer coatings based on ED-16 on the type and content of organic-mineral fillers: 1 - graphite; 2 - soot; 3 - titanium oxide.



a) *b)*

1-kaolin; 2- soot; 3- talc

Fig. 2. Dependence of adhesive strength (a) and microhardness (b) of anticorrosive composite epoxy polymer coatings based on ED-20 on the type and content of organic-mineral fillers

As can be seen from the presented results, the dependence of the adhesive strength and microhardness on the content of fillers has an extreme character. The adhesive strength increases with an increase in the content of kaolin up to 80 mass.p.., soot up to 40 mass.p., talc up to 40 mass.p., zinc oxide up to 25 mass.p., in the composition of coatings based on ED-16 or ED- 20. A further increase in the content of this filler, and their high dispersion play the role of a center in the preparation of compositions and the curing process ends with higher degrees of crosslinking.

The greatest increase in the microhardness of coatings is observed with the introduction of such fillers as kaolin, zinc oxide and titanium. This is obviously due to the fact that, due to the greater mobility of the structural elements, a more ordered structure of densely packed polymer chains is formed near the filler particles. With a further increase in the content of fillers, a decrease in adhesive strength and microhardness is observed. This nature of the dependence of adhesive strength and microhardness on the content of fillers is due to the fact that with a high content of fillers, their uneven distribution leads to a decrease in density in other indicators. In addition, the presence of highly polar functional groups in the composition of mineral fillers enhances their interaction with the binder, which contributes to the formation of stronger physical bonds between the filler and the polymer. An increase in the content of titanium oxide and zinc increases the strength and corrosion resistance of the composition due to the formation of a metal coordination bond [9, 12, 14].

The extreme nature of the change in strength properties can also be explained by the molecular interaction between the polymer and the filler, which occurs between the active and functional groups of epoxy oligomers and fillers due to chemical interaction with the formation of strong chemical bonds.

Based on the above principles and the results of our research [1, 2, 9], new compositions of effective anticorrosive composite materials and coatings based on organic-mineral fillers were developed. The composition of the investigated epoxy anti-corrosion polymer compositions (APC) is shown in Table 1.

Table 1. Compositions of the developed anti-corrosion polymer compositions

Components	**Content components, %**		
	APC-1	APC-2	APC-3
Epoxy oligomer ED-16 or ED-20	60 ED-16	55 ED-20	50 ED-16 1:1 ED-20
gossypol resin	15	20	25
PEPA	12	12	12
zinc oxide			5
talc		4	3
graphite	4		
kaolin		4	
soot	5	5	5
titanium oxide	4		

IR spectroscopic studies of the developed anti-corrosion polymer composite materials and coatings based on the ED-16, ED-20 oligomer and other organic-inorganic ingredients were carried out, which are shown in Figure 3-5.

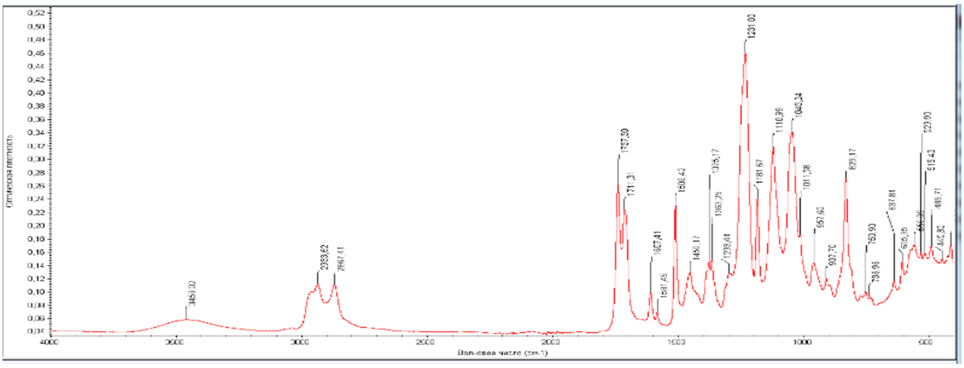


Fig. 3. IR spectrum of the developed anticorrosive polymeric composite material APC-1 based on the ED-16 oligomer

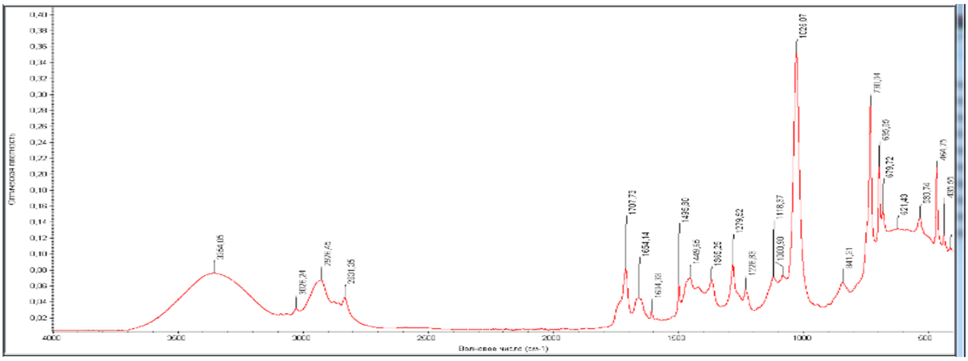


Fig. 4. IR spectrum of the developed anticorrosive polymeric composite material APC-2 based on the ED-20 oligomer

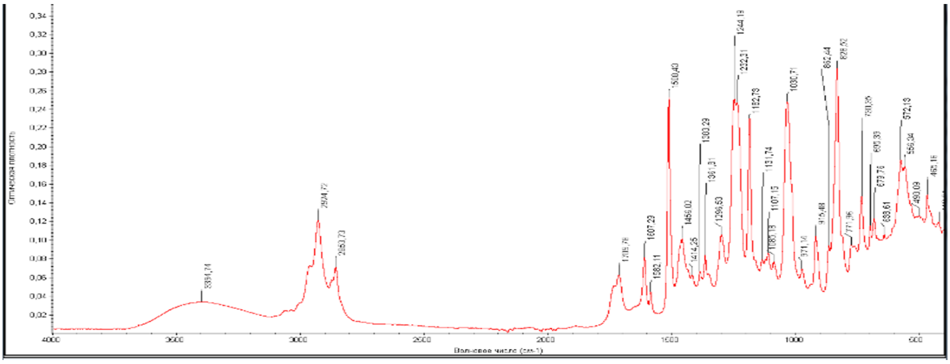


Fig. 5. IR spectrum of the developed anticorrosive polymeric composite material APC-3 based on ED-16 1:1 ED-20 oligomers

As can be seen from the IR spectrum of the developed anticorrosion epoxy polymer composite materials (Fig. 3-5), in the composition of this composition, a change in the degree of absorption is observed in the regions 3458, 3354, 2926, 2853, 1580, 1490, 1350, 1000, 489 cm $^{-1}$ due to the presence of –C=O, -COOH, - NH, - NCO, -C-OH, Zn-O-C, Ti-O-C groups. The introduction of zinc oxide and titanium oxide as a filler affects the structure of the polymer matrix of the epoxy resin and leads to an increase in the intensity of the peaks. This suggests that a chemical reaction occurs between the hydroxyl, carboxyl, and amine groups of the modified epoxy polymer compositions with fillers due to valence and deformation bonds.

Composite epoxy polymer anticorrosion materials with the above fillers form thermosetting compositions that have valuable properties such as high adhesion to the surface of the material on which they are cured, high mechanical strength, good chemical resistance and water resistance, do not emit volatile products during curing and are characterized by low shrinkage (up to 2 ,5%).

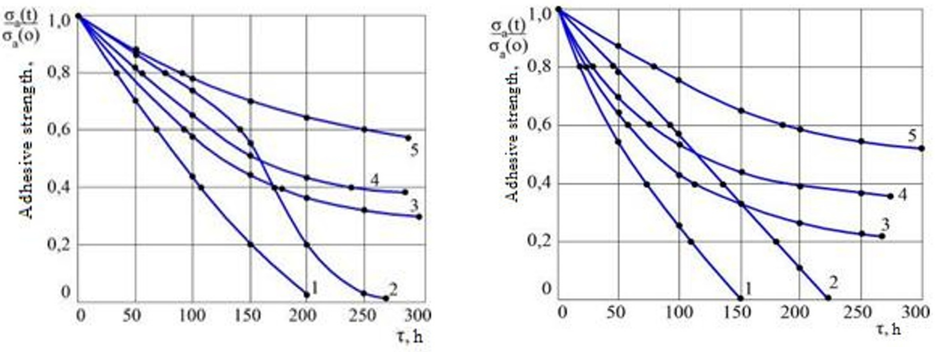
High physical, mechanical and operational properties of the developed anticorrosion epoxy coatings, which distinguish them from many others, are determined by the structure of their molecule.

The protective effect of composite epoxy coatings is determined by the ability to inhibit chemical and electrochemical reactions on the metal surface, slow down the diffusion and transfer of corrosive agents, electrochemically protect or passivate the metal due to the introduction of pigments or corrosion inhibitors, as well as adhesion and deformation-strength properties of coatings [16- 18].

It has been established that the effectiveness of protection also depends on the surface preparation method, application method, film thickness, type of coating system components, and other factors [19-20].

Composite polymeric materials intended for use in aggressive environments in the form of a coating, as already noted above, in addition to anticorrosion properties, must also have high adhesive properties to metal surfaces, especially in aggressive environments.

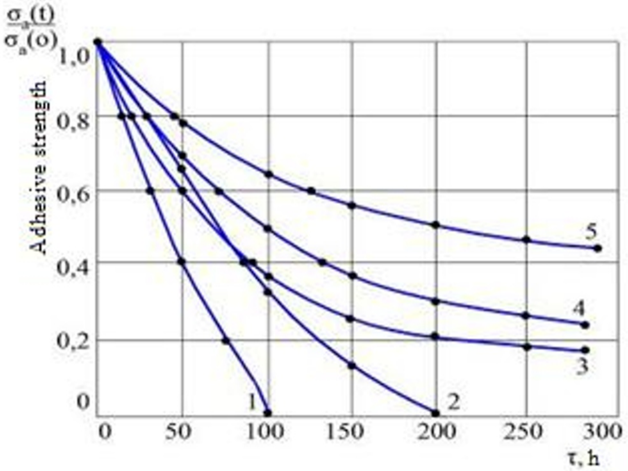
The effect of aggressive media on the change in the adhesive properties of epoxy composite materials to steel substrates has been studied. Under the action of aggressive media, the change in the properties of materials is not the same at all points of the obtained samples. In this case, the intensity of the destruction of the material depends on the concentration and a number of other parameters. When studying the chemical resistance of composite materials used as a coating, as noted above, one of the important criteria for assessing their resistance is the change in adhesive strength under exposure to aggressive media (Fig. 6-7).



a) *b)*

1-50% CH_3COOH, 2-40% HNO_3, 3-25% HCl, 4-H_2O, 5-40% H_2SO_4

Fig. 6. Changes in the adhesive strength of APC-1 (a) and APC-2 (b) coatings to a steel substrate in various aggressive media



1-50% CH_3COOH, 2-40% HNO_3, 3-25% HCl, 4-H_2O, 5-40% H_2SO_4

Fig. 7. Changes in the adhesion strength of APC-3 coatings to a steel substrate in various aggressive environments

The use of this criterion is especially effective in assessing the protective properties of coatings, since the change in adhesion is a comprehensive assessment of a number of properties, such as diffusion permeability, internal stresses. Analyzing changes in adhesive strength (Fig. 6 and 7), one can judge the permeability of coatings, the nature of the chemical interaction between the substrate and the aggressive environment.

Figures 6 (a, b) and 7 show that the nature of the change in the adhesive strength of epoxy compositions based on ED-16 and ED-20 from the interaction of aggressive media is almost identical. The adhesive strength of these coatings in all cases decreases: in sulfuric acid by 60, in water by 40, hydrochloric acid by 55% relative to the value in air when kept in these environments for more than 10 days. The same coatings completely lose their adhesive strength in nitric and acetic acids within 10 and 6 days.

In this process, the destruction of metals occurs in the environment of various electrolytes , that is, an atom is removed from the crystal lattice, which is accompanied by the appearance of an electric current inside the system. Under the influence of acids, corrosion of metals with hydrogen or oxygen depolarization :

Hydrogen depolarization carried out on the cathode during electrochemical corrosion in an acidic environment (in the environment of hydrochloric, sulfuric, nitric and acetic acids):

$$2H^{+} + 2e^{-} = H_2$$
$$2H_3O^{+} + 2e^{-} = H_2 + 2H_2O$$

Oxygen depolarization is also carried out on the cathode during electrochemical corrosion only in a neutral medium, in our case in water:

$$O_2 + 4H^{+} + 4e^{-} = H_2O$$
$$O_2 + 2H_2O + 4e^{-} = 4OH$$

When this happens, the restoration of dissolved oxygen and the destruction of polymers proceeds at the interface between the phases of the polymer - substrate.

Studies of the chemical destruction of a coating based on ED-20 in hydrochloric acid, carried out using IR spectroscopy, showed that under the action of an aggressive medium, the film-forming material undergoes significant structural changes (Fig. 8). They are expressed in the formation of a large number of intermediate and final products of interaction.

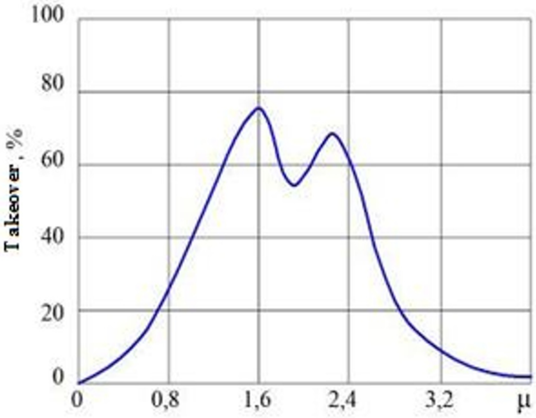


Fig. 8. Dependence of the main absorption band of HCl close to the infrared region

An analysis of the surface spectra showed that on it, in the process of electrochemical corrosion, in which the metal is simultaneously oxidized, the corrosion medium is restored. In this case, the same chemical compounds arise as in the bulk, but their number is approximately an order of magnitude greater. Therefore, it can be assumed that the processes of chemical destruction, as well as mechanical destruction, develop on the surface of the material and depend on the phenomena occurring in the layer boundary with the medium. The complexity of studying the chemical destruction of a material under the action of aggressive media is associated with diffusion processes in it.

It has been established that the introduction of mineral fillers into the composition of epoxy compositions [9], despite the decrease in electrical resistivity under aggressive conditions, these filled epoxy polymer compositions retain their adhesion strength well, which can significantly improve their anticorrosion properties. With this in mind, we have developed an effective composition of anti-corrosion compositions for obtaining protective coatings from them, as noted above, conventionally named APC-3. Table 2 shows the main physical, chemical and mechanical properties of the developed composite anti-corrosion material APC-3, operating in various aggressive environments.

Table 2. Basic physical, chemical and mechanical properties of the developed Anti-corrosion coating - APC-3

Properties		Indicators
1	Modulus of elasticity in bending E_{bend}, MPA	3000-3200
2	Limit of bending strength, a_{bend}, MPa	6.7-7.4
3	Heat resistance according to Vicat, K	355-360
4	Dielectric constant, ε	6.8-7.0
5	Specific surface electrical resistance R, 10^{14} Ohm	31.8
6	Adhesion strength 0_{ad}, MPa	8.2-9.0
7	Microhardness H_M 1MPa	20-30
8	Thickness not less than, mm	0.2-0.3
9	Specific volume electrical resistance Q, 10^{14} Ohm cm	17-18
10	Chemical resistance coefficient	
	after 30 days in: 50% CH_3COOH	0.68
	40% HNO_3	0.71
	25% HCl	0.74
	40% H_2SO_4	0.78
	in water	0.76

4 Conclusions

Thus, effective compositions of anticorrosive composite polymeric materials and coatings based on epoxy oligomers ED-16 and ED-20 and organo-mineral fillers were developed to prevent corrosion of metals operating in aggressive environments. Therefore, the addition of the above fillers has a positive effect on the anticorrosion properties of composite materials based on ED-16 and ED-20, and also slows down the diffusion of aggressive media and increases the adhesive strength, which leads to an increase in the durability and corrosion resistance of the resulting coatings based on them.

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