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Investigation of Corrosion Resistance of Two-Layer Protective Coatings

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Abstract

In this article, the influence of aggressive environments on a two-layer coating was investigated. Modern industry places high demands on quality control methods and coating properties during operation. It was established that the electrical resistance of epoxy composite samples depends significantly on the nature of the filler, the cohesive strength of the coatings, and the ambient temperature. We have determined the initial values of the volume resistance of epoxy composites and the temperature values when the samples lose their dielectric properties. The effectiveness of the use of electrospark water hammer treatment with the subsequent introduction of a bidisperse filler at optimal concentrations, which will increase the resistance of protective coatings, is shown.

KEY WORDS: *Polymer composite coatings, polyethylene polyamine, polymer matrix, epoxy composites*

1. Introduction.

Improvement of the quality of operation and durability of technological equipment for chemical, food and oil refining industries under the influence of aggressive environments is directly related to the reliability of anti-corrosion protection of metal surface parts. Polymer composite coatings (CC), including those based on epoxy binder, are of great importance in the complex of anti-corrosion methods of technological equipment protection. Their wide application is due to the availability and low cost of ingredients in the composite formation, and manufacturability when applied to complex surfaces [1]. Modern industry has high requirements for quality control methods and coating properties during operation. While developing CC the measurement of potential, current, resistance, capacity, their volt-ampere characteristics are taken into account. Determination of the mass change in the test sample is advantageous in this direction [2]. The given laboratory research methods do not allow to assess the protective properties (CC) sufficiently, as the nature of internal stresses distribution in the material, concentration, filler nature, interfacial adhesion interaction and operating temperature of polymer composites significantly affect their corrosion resistance.

2. Materials and equipment

In order to create the coatings, epoxy diane resin of ED-20 (GOST 10587-84) grade was used. Polyethylene polyamine (PEPA) hardener (TU 6-05-241-202-78) was introduced into diane resin, the fillers were thoroughly mixed and introduced. The concentration of the dispersed filler varied from 0 to 100 wght. p. per 100 wt. p. of epoxy binder. The formation of composite material for coatings was carried out according to the following temperature modes: harderning at room temperature for 24 hours, followed by heat treatment at $T = (393 \pm 2)$ K temperature for 2 hours. Further, the samples were kept at room temperature for 48 hours. Then, the tests were carried out.

3. Investigations

While studying the corrosion processes and performance properties of protective coatings, a comprehensive approach to their investigation, covering a wide range of established procedures is effective from the scientific and practical point of view. The phenomena of diffusion, sorption and dielectric characteristics of heterogeneous materials and coatings made of them should be taken into account.

According to papers [2-4], the increase in adhesive strength at the phase boundary "protective coating - metal

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base" and corrosion resistance is achieved by using a thin intermediate layer of polymer, which significantly enhances the interaction between the polar groups of the adhesive and the substrate. Therefore, while forming the adhesive layer, based on the results of previous investigations the effect of concentration and nature of the dispersed filler on electrical resistance of samples during the temperature increase, were investigated at the initial stage of creating protective anti-corrosion coatings. It should be noted that the polymer matrix was formed on the basis of modified by electrospark hydraulic impact (ESHI) epoxy resin and aliphatic resin DEG-1was used as plasticizer [5].

It is determined experimentally (Fig. 1.1) that the electrical resistance of epoxy composite samples significantly depends on the nature of the filler, the coatings cohesive strength and the ambient temperature. While investigating the epoxy matrices, it is found (Fig. 1.1, a) that if the temperature increases, the electrical resistance decreases. However, at oligomer ESHI the increase in electrical resistance by 1.7 times compared to the original matrix is observed. Electrospark hydraulic impact involves the mechanocracking of macromolecule chains and the formation of free radicals, which in turn form new physical and chemical bonds in the coatings formation. With temperature increase, in epoxy coatings investigations, a significant decrease in electrical resistance to the point where the sample loses its dielectric properties is observed. For untreated oligomer, this temperature is 365 K, and for treated ESHI material it is 371 K. It makes it possible to confirm that matrix treatment by electrospark hydraulic impact results in the improvement of dielectric and, consequently, anticorrosive properties of CC.

The next step is the investigation of electrical resistance of composites containing disperse fillers at different concentrations. It is proved (Fig. 1.1 b, c, d) that when the filler is introduced into the oligomer, the improvement in composites dielectric properties in comparison with the initial matrix is observed. It is determined that for aluminium oxide (Fig. 1.1, b) the optimal concentration for the increase of dielectric and anticorrosive properties of CC is 30 wght. p. of the filler per 100 wght. p. ED-20.

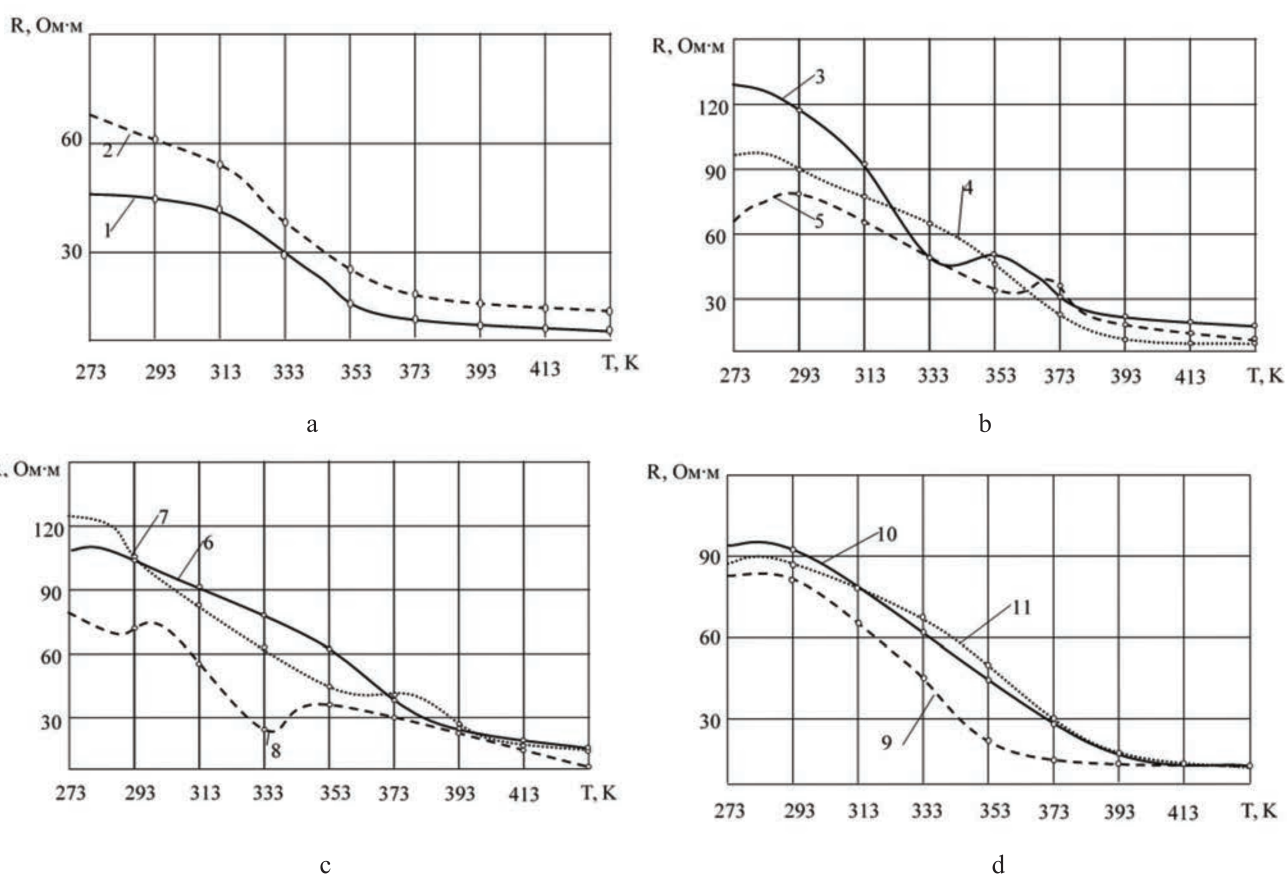

Fig.1 The effect of filler concentration (wght. p. per 100 wght. p. of ED-20 epoxy oligomer and 10 wt. p. of DEG-1aliphatic resin) and temperature on the samples electrical resistance after epoxy resin treatment by electrospark hydraulic impact: a) 1 - untreated matrix; 2 - treated matrix by electrospark hydraulic impact; b) 3 - composite containing aluminium oxide (30 wght. p.); 4 - composite containing aluminium oxide (50 wght. p.); 5 - composite containing aluminium oxide (80 wght. p.); C) 6 - composite containing chromium oxide (30 wt. p.); 7 - composite containing chromium oxide (50 wt. p.); 8 - composite containing chromium oxide (80 wght. p.); d) 9 - composite containing soft thermal carbon (30 wght. p.); 10 - composite containing soft thermal carbon (50 wght. p.); 11 - composite containing soft thermal carbon (80 wght. p.).

With the increase of the given filler concentration, the decrease in electrical resistance by 1.4… 2.1 times is observed. Further investigations proved that while using dispersed particles of chromium oxide and soft thermal carbon, the optimal filler concentration is 50 wght. p. per 100 wght. p. of ED-20 epoxy oligomer. Analysis of the above mentioned experimental results of the investigation is presented in Table 1.1. We established the initial values of the volume resistance of epoxy composites and the temperature values when the samples lose their dielectric properties. The correlation between the indicated characteristics of the investigated composites was experimentally established: higher initial values of the samples electrical resistance correspond to higher temperature values of CC dielectric properties loss.

It is determined experimentally that the material with the following composition has the greatest adhesive strength - 50 wght. p. per 100 wght. p. of ED-20 and 10 wght. p. of DEG-1plasticizer. It should be noted that the obtained results are in good agreement with the experimental investigations of adhesive strength of these composites after matrix modification by ESHI [6]. In particular, it was found that the maximum indicators of adhesive strength are the composites containing chromium oxide particles at concentration of 50 wght. p. per 100 wght. p. of ED-20.

Table 1

Investigation of materials dielectric properties.

Fillers		ESHI treatment	Initial volume resistance at 293 K, R, Ohm • m	Temperature at which the composite loses its dielectric properties(R<20Ohm·m), K
Type of filler	Filler concentration, q, wght. p.			
matrix	-	-	42.05	365
matrix	-	+	73.24	371
aluminium oxide	30	+	13.86	381
	50	+	95.92	383
	80	+	64.23	382
chromium oxide	30	+	113.02	401
	50	+	123.63	391
	80	+	77.26	361
soft thermal carbon	30	+	85.83	382
	50	+	94.74	390
	80	+	89.35	375

Note: + oligomer treatment by electro spark hydraulic impact; - without treatment.

The next stage of the investigation is to determine the optimal ratio of components in the material of the working (surface) layer and to evaluate the behavior of composites containing disperse filler in aggressive environments. It should be noted that on the basis of the previous investigations, the optimal concentrations of bidispersed filler in composites with high dielectric characteristics are selected. In order to determine the optimal concentrations of the main and additional fillers and to optimize the CC formation modes, the method of multifactorial experiment planning is used in this paper.

Previous investigations of physical-mechanical, thermophysical and adhesive properties have shown that for all selected fillers pre-treatment by ESHI matrix provides the increase in these characteristics by 1.8 ... 3.4 times (depending on the chemical nature and concentration of the filler). However, taking into account the optimal concentration of the selected fillers, it was considered that, in general, the increase of these characteristics was by 2.4 times.

Taking into account the fact that protective coatings are planned to be implemented in order to protect the technological equipment of chemical and food industries, CC durability to the impact of aggressive environments on the example of mineral oils is chosen as the optimization criterion. As the result of the carried out experimental researches the values of corrosion resistance characteristics to mineral oils at various concentrations of the main and additional fillers, as well as at treatment by EIGU matrix are obtained.

Analysis of the investigation results showed that the best characteristics of relative permeability have coatings of epoxy resin ED-20 - 100 wght. p., aliphatic resin DEG-1 -10 wght. p., the main filler ferrite and additional soft thermal carbon. It should be noted that the electrospark hydraulic impact treatment improves the relative permeability of all, without exception, CC.

The corrosion resistance of the system "carbon steel (Article 3 - protective coating) in aggressive environment

(3% sodium chloride solution) was investigated by the method of impedance spectroscopy (Tables 1.2, 1.3). It should be noted that the bidisperse filler concentration was selected on the basis of the research results.

Table 2

Time changes of protective coatings resistance at 1 kHz frequency in 3% sodium chloride solution

Material	Filler concentration, q, wght. p.	Time change of resistance R, Ohm·sm^2							
		τ, 24-hour periods							
		0	20	40	60	80	100	120	140
Matrix	-	7.85	6.45	4.45	4.5	4.42	4.40	4.32	4.28
$SiC+Al_2O_3$	80+80	6.91	6.05	5.21	5.19	5.24	5.36	5.43	5.40
$B_4C+Cr_2O_3$	80+50	6.86	5.20	5.67	5.61	5.63	5.70	5.72	5.71
ferrite + soft thermal carbon	80+80	7.03	6.43	6.45	6.29	6.21	6.29	6.52	6.64

According to the results of impedance investigations at 1 kHz current frequency at the beginning of the tests, the coatings resistance is within the range of 6… 8 Ohm × sm2. In this case the dispersed coatings have slightly lower resistance compared to the epoxy matrix, which indicates their reduced electrochemical activity. Exposure of the samples in aggressive environment for 20… 40 days showed a significant decrease of the epoxy matrix resistance, with the difference of 45%. It is found that the resistance of coatings filled with ferromagnets ferrite and, in addition, soft thermal carbon, is 0.93 ... 1.25 times higher than the resistance of composites containing other particles (Table 1.2). While increasing the duration of coatings exposure in aggressive environment (60… 100 days), the equilibrium process of electrolyte penetration to the metal surface is established, in this case the resistance is almost unchanged. The investigations show that after the samples' exposure in aggressive environment for 100 days, the resistance of these coatings begins to increase monotonically. This is explained by the lack of diffusion of aggressive environment due to the slight protective coatings swelling, as well as the presence of the adhesive layer in the coatings, which provides both adhesive and anti-corrosion properties of CC. In addition, physical-mechanical investigations of composite materials for compression, bending and toughness confirmed the increase of the above-mentioned indicators by 1.25 times in coatings with additional adhesive layer in comparison with the original investigated coatings. At the same time, the relaxation of internal stresses in the protective coatings during their operation and maintaining their high adhesive and cohesive strength makes it possible not only to preserve but also to improve the protective properties of CC.

Table 3

Time change of protective coatings capacity at 1 kHz frequency in 3% sodium chloride solution

Material	Filler concentration, q, wght. p.	Time change of capacity C, pF/sm^2							
		τ, day							
		0	20	40	60	80	100	120	140
Matrix	-	64	112	178	187	182	181	178	179
$SiC+Al_2O_3$	80+80	112	155	154	155	161	169	165	171
$B_4C+Cr_2O_3$	80+50	115	130	125	137	145	146	147	149
ferrite + soft thermal carbon	80+80	82	149	123	128	132	127	126	120

In order to confirm the reliability of the obtained results, additional analysis of electrical capacity of the protective coatings is carried out (Table 1.3). It has is determined experimentally that during exposure in corrosive medium, the electrical capacity of CC increases due to the change of dielectric constant of the matrix material as a result of sorption (Table 1.3). When the medium reaches the steel surface, the coating capacity increases step-wise due to the occurrence of electrochemical component [7]. It is shown that up to 60 days the capacity of samples from the polymer matrix reaches maximum values and increases insignificantly with the research increasing duration. For coatings containing dispersed particles of ferrite and soft thermal carbon, the capacity growth is significantly slower compared to other coatings, and only after 120… 140 days the capacity reaches the values of 170… 180 pF/sm2, typical for the beginning of coatings damage.

4. Conclusion

From the experimental results of complex studies of the corrosion durability of KP, the optimal content of polydisperse filler was established, which allows to significantly improve the operational properties of technological equipment of the chemical industry

From the experimental results of the complex investigations of corrosion resistance of CC, the optimum content of polydisperse filler which makes it possible to increase considerably the operational properties of chemical industry technological equipment is determined. The analysis of the obtained results enables to confirm the influence of interphase physical-chemical interaction on the polymer composites corrosion resistance, which can be regulated by scientifically substantiated selection of the disperse filler, its concentration and ratio. The efficiency of matrix treatment by electrospark hydraulic impact with subsequent introduction of the disperse filler at optimal concentrations is shown. This makes it possible to increase the protective coatings resistance by 0,93...1,24 Ohm × sm2, and also provides significant reduction in capacity (by 29 ... 51 pF/sm2). The additional use of adhesive layer in the developed coatings provides, along with the improvement of the adhesion of polymer composites to the metal base, the improvement of physical-mechanical and anticorrosive properties of the composites. It should be noted that the application of the developed protective coatings is also effective when used to protect the equipment operating at elevated temperatures. In this case, the electrical resistance during operation changes insignificantly.

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