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INNOVATIVE TECHNOLOGIES IN CORROSION-RESISTANT COATINGS DEVELOPMENT AIMED AT SHIP NAVIGATION EQUIPMENT PROTECTION

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Summary. *The efficient use of some innovative technologies in adhesives with advanced operational characteristics development aimed at anti-corrosion properties increase of transport means has been substantiated in the paper under discussion. The above-mentioned technologies involving the use of some interaction-active ingredients forming the cross-linkable coatings composition, including some polymers, have provided their cohesion properties essential improvement. Epoxy diane oligomer ED-16 has been chosen as the main component for the matrix in the composite formation. The aliphatic resin DEG-1 (GOST 10136-77) as a plasticizer has been added to the epoxy oligomer. The compound has been formed of the following concentration: epoxy resin ED-16 : plasticizer DEG -1 – 100: 40. The hardener of cold hardening polyethelenepolyamine PEPA (ТУ 6-05-241-202-78) has been used at the epoxy resin-based developed materials polymerization. Phthalic acid anhydride has been used as a modifier to improve the properties of epoxy composite materials. The modifier was added to the matrix in the following ratio: from 0,10 to 2,00 pts.wt. per 100 pts.wt. of epoxy oligomer ED-20. The molecular formula of the modifier is as follows: $C_8H_4O_3$. Molar mass is 148,1 g/mol. Density is ρ = 1,52 г/см³. To form a composite material or a protective coating with some improved adhesive properties and inconsiderable residual stresses the phthalic acid anhydride as a modifier was found to be added to the epoxy matrix with the content q = 1,25 pts.wt. per 100 pts.wt. of the epoxy matrix (oligomer ED-20 + plasticizer DEG -1). In this case, the adhesive strength of the coating is being increased from σ_a = 28,3 MPa to σ_a = 46,4 MPa, and residual stresses – from $\sigma_з$ = 1,9 MPa to $\sigma_з$ = 2,1 MPa. First of all, the improved properties of the modified materials were caused by the interaction of active carbonyl (C=O) groups of the modifier with nitrogen-containing (NH-) groups of the hardener. It has provided the increase of the composite cross-linking degree resulted in their both adhesive and cohesion properties improvement. Moreover, it was found that the modifier use in the compound with the content q = 1,0…1,5 00 pts.wt. per 100 00 pts.wt. of the matrix has provided the increase of the river water influenced coatings resistance from ρ = 12,1 Om·cm² до ρ = 21,2…22,4 Om·cm². Though, some further increase of the additive content in the coating has caused the deterioration of anti-corrosion characteristics of the materials. Thus, the conducted study has contributed to the determination of the most efficient content ratio of phthalic acid anhydride as a modifier to for the coatings of functional use.*

Key words: *composite, adhesive, corrosion, coating, innovative technologies.*

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Problem statement. It is well known [1–4], that the ship navigation equipment is constantly influenced by an aggressive impact of the environment. It has resulted in the early ageing of machine parts and mechanisms and has caused their failure. In this case, the use of some innovative technologies dealing with development of adhesives with advanced operating characteristics aimed at anti-corrosion properties of transport means is quite promising direction. The above-mentioned technologies have involved the use of interaction-active ingredients in the coatings composition which provide the essential improvement of their cohesive properties at the coatings cross linking, including the polymers case.

Analysis of the latest studies and publications. The authors [5, 6] have shown, that nowadays some innovative technologies of polymer composite-based anti-corrosion coatings formation and use have been widely spread. Moreover, the above-mentioned materials and the protective coatings based on them have been formed on the basis of epoxy oligomers ED-16,

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ED-20, ED-22. Here, the use of epoxy matrix based on epoxy resin ED-20 is quite promising direction as the materials on its basis have advanced adhesive and cohesive properties providing the improvement of anti-corrosion characteristics of new composites.

It should be mentioned, that to improve the materials properties some modifiers and plasticizers must be added to the epoxy matrix. On the one hand, it will make possible to improve the materials plasticity, and on the other hand – to form the compounds with advanced operating characteristics in general. Thus, the combination of active components and the most efficient concentrations in the protective coatings has been an important direction of new technologies development on the creation of materials with the required properties.

Paper purpose – to apply some innovative technologies due to the components' optimization at the protective coatings' formation for the ship navigation equipment.

Materials and technique of the research. The epoxy diane oligomer ED-16 (GOST 10587-84) was used as a base in the polymer matrix formation. In addition, the aliphatic resin DEG-1 (GOST 10136-77) as a plasticizer has been added to the epoxy oligomer. The compound was formed of the following concentration: epoxy resin ED-16: plasticizer DEG -1 – 100: 40.

A hardener of cold hardening polyethelenepolyamine PEPA (TU 6-05-241-202-78) has been used in polymerization of the developed materials based on epoxy resin.

The phthalic acid anhydride (PAA) was used as a modifier for the epoxy composite materials (CM) properties improvement. The modifier was applied to the matrix with content from 0,10 to 2,00 pts.wt. per 100 pts.wt. of epoxy oligomer ED-20. The molecular formula of the modifier: $C_8H_4O_3$. The molar weight of MA – 148,1 g/mol. It looks like white cereals. Density – $\rho = 1{,}52$ g/cm³. Temperature of melting – $T = 131{,}6$ °C. Temperature of boiling – $T = 295$ °C. The scheme of chemical bonds of phthalic acid anhydride as a modifier is shown on fig. 1.

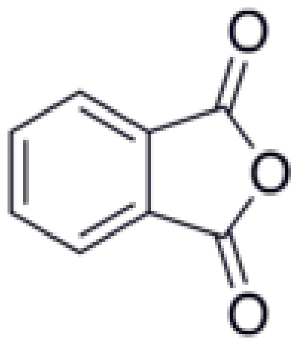

Figure 1. Scheme of chemical bonds of phthalic acid anhydride as a modifier

Epoxy composites have been formed by the following technology: the resin was heated to the temperature $T = 353 \pm 2$ K and the exposure at the given temperature within the time interval $\tau = 20 \pm 0{,}1$ min; hydrodynamic shift of oligomer and the fractures of filling within the time interval $\tau = 1 \pm 0{,}1$ min; ultrasound treatment (UST) of the composition within the time interval $\tau = 1{,}5 \pm 0{,}1$ min; the composition cooling till the room temperature within the time interval $\tau = 60 \pm 5$ min; the hardener applying and the composition mixing within the time interval $\tau = 5 \pm 0{,}1$ min. The CM was hardened by the mode: during the time interval $\tau = 10{,}0 \pm 0{,}1$ год at temperature $T = 303 \pm 2$ K. After that they were heated up to the temperature $T = 413 \pm 2$ K, were exposed during time interval $\tau = 2{,}0 \pm 0{,}05$ h were cooled to the temperature $T = 293 \pm 2$ K.

The impact of a modifier content on adhesive properties of composites on the metal surface has been studied. Moreover, the fracture stresses have been calculated («method of mushrooms») under the homogeneous separation conditions of the glued pair of patterns according to GOST 14760-69 (Fig. 1). The adhesive strength was studied on an automatic tensile testing machine UM-5 at speed of loading υ = 10 N/s. The diameter of steel patterns working area was equal to d = 25 mm.

The residual stresses were studied by a console method.

The corrosion resistance of the protective coatings has been studied under laboratory room conditions and according the results the temporal change in the patterns resistance influenced by the aggressive environments was analyzed. To measure the resistance of the protective coatings a device RCL-meter of type E7-22 was used. The device was connected to a measuring cell where the patterns in the form of the coatings surfaced on the metal base were located. Some glass cylinders of diameter d = 25 mm filled with sea water (TUU 006: 2011) were glued on the coatings. The coatings resistance was measured for 30 days at temperature $T = 293 \pm 2$ K whose values were calculated by the formulae: $\rho = R \cdot S$, Om; $S = \pi D^2/4$, cm^2. To obtain some average values of the coating resistance and capacity not less than 5 patterns have been used whose working area was 4,9 cm^2.

Results of the study and their discussion. During the initial stage the study aimed at molecular mass determination of the synthesized modifier has been carried out by mass-selective detection of gas chromatographic method.

In this case the substance of mass 0,0124 g was dissolved in methanol and the chromatographic analysis was made under the following conditions:

- device – GC/MS Agilent Technologies 6890 N;
- capillary column – HP 19091S-433 (HP-5MS);
- length – 30 mm, diameter – 0,25 mm, phase – 0,25mkm;
- gas-carrier – helium;
- constant flow of gas-carrier – 1,5 ml/min;
- injector – autoinjector 7683, Split 20:1;
- temperature of evaporator – T = 250 °C; technological modes of heating: Tstart = 100 °C, retention – 2 min, speed of heating – 15 °C/min, T_{finish} = 280 °C;
- detector – mass-selective, temperature of interface T = 280 °C;
- ionization by electronic impact, ionization energy – 70 eV
- ion source temperature – T = 230 °C;
- temperature of quadrupole – T = 150 °C;
- sample – 1,0 mkl.

Experimental results of the tests are shown on fig. 2. On the previous stage the chromatographic analysis of the modifier samples was made and the signals values have been found since their retention. On the next stage the parameters of signals were analyzed. As a result, the signal was obtained at retention time t = 7,73 c (fig. 2).

Then we have found the dependence of the values of characteristic signals on m/z (m – the sample mass; z – charge) for the signal specified retention time RT = 7,73 mAU which characterize only the substance under study, i.e. synthesized modifier. As a result, we have found the values of characteristic signals, the biggest 10 peaks have been found at m/z = 37,8; 38,1; 50,4; 74,19; 75,12; 76,8; 77,8; 104,9; 105,7; 148,3. We have compared the obtained values with the table ones and due to this we have found the structural formula and the value of molecular mass of the synthesized modifier. It has been proved that the modifier formula looks like: $C_8H_4O_3$. The molecular mass of phthalic acid anhydride is equal to 148,16044.

The molecular mass of phthalic acid anhydride almost coincides with the same mass of the hardener and does not differ considerably from the molecular mass of epoxy oligomer. In our opinion, this is an important aspect of the directional arrangement of the processes dealing with polymer compounds structure formation. Such structural characteristics and available active groups in the modifier will make possible to increase the degree of eco-composites cross-linking and as a result to improve their adhesive and cohesive properties.

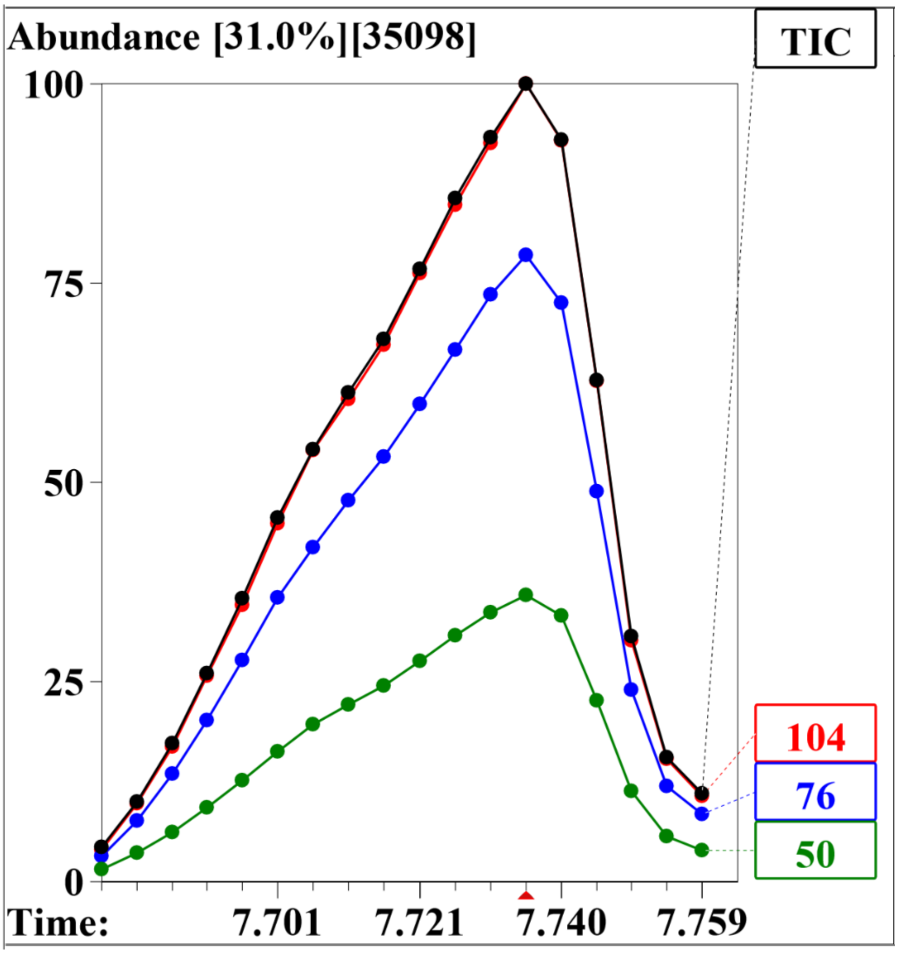

Figure 2. Curves of signals values dependence on the retention time of the modifier sample (within time interval t = 7,70…7,76 c)

It is generally known, that one of the most important properties of protective polymer coatings has been their adhesive strength and residual stresses. We should mention, that the dynamics of the specified characteristics indices depending on the modifier PAA content has been studied in the paper under discussion. The epoxy matrix was formed by the following concentration of the components: epoxy resin ED-16: plasticizer DEG-1 – 100 : 40.

The conducted experiments have proved (fig. 3), that adhesive strength for the plasticized epoxy matrix is equal to σ_a = 28,3 MPa. The application of a modifier to the matrix has caused an essential increase of adhesive strength values in case of separation from the epoxy matrix. In particular, it is shown (fig. 3, curve 1), that the application of phthalic acid anhydride under its inconsiderable content conditions (q = 0,50…0,75 pts.wt.) has provided an increase in the matrix adhesive strength values from σ_a = 28,3 MPa to σ_a = 40,1…44,3 MPa. The maximum value on the adhesive strength influence curve on the modifier concentration (σ_a = 46,4 MPa) was observed at the content of the latter in the coatings q = 1,25 pts.wt. Any further increase of the additive content in the material has resulted in some deterioration of adhesive properties of the developed materials.

The improvement of properties of the modified phthalic acid anhydride materials, first of all, was caused by the interaction of active carbonyl (C=O) groups of the modifier with nitrogen-containing (NH-) groups of the hardener. It has provided the increase of the composites cross linking degree and, as a result, has improved their adhesive and cohesive properties.

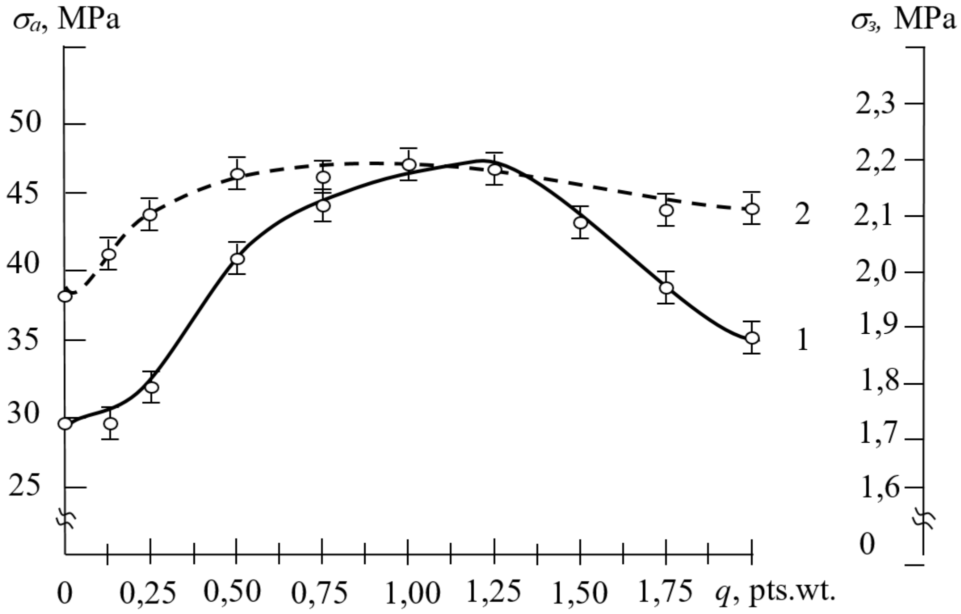

Figure 3. Curves of adhesive strength and residual stresses in CM vs the PAA as a modifier content: 1 – adhesive strength at separation (σ_a); 2 – residual stresses ($\sigma_з$). Material of the base – steel of St 3 grade

Residual stresses are one more property defining the durability of transport means coatings. So, along with the tests on adhesive strength of the modified materials some additional studies on their residual stresses' values were conducted. The conducted experiments have proved (fig. 3, curve 2) that the residual stresses in the initial epoxy matrix equal to $\sigma_з$ = 1,9 MPa.

The additive application irrespective of the concentration has provided the increase of residual stresses from $\sigma_з$ = 1,9 MPa to $\sigma_з$ = 2,1 MPa. One can state, the modifier has provided not only an increase of adhesive strength of the modified materials, but has contributed to some extra increase of residual stresses. It means, that such materials have advanced adhesive and cohesive properties in complex in comparison with the initial epoxy matrix. We have come to this conclusion due to the fact that the residual stresses are indirectly a criterion of the material strength determined by the degree of their cross linking.

On the final stage the anti-corrosion properties of the developed materials were studied. Dynamics of the coatings' specific resistance of their 30 days staying under river water conditions was chosen as a criterion of corrosion resistance. The following materials were studied: epoxy matrix (test sample), coatings with a modifier for which the maximum values of adhesive strength were obtained in advance. The conducted experiments have proved (fig. 4), that only plasticized epoxy matrix has been characterized by minimal values of specific resistance among all the samples under study. Its value of specific resistance is ρ = 12,1 Om·cm^2. The modifier application to the compound of content q = 1,0…1,5 pts.wt. per 100 pts.wt. of the matrix has provided an increase of resistance of the coatings under river water conditions from ρ = 12,1 Om·cm^2 to ρ = 21,2…22,4 Om·cm^2. Any further increase of the additive content in the coating has resulted in some deterioration of anti-corrosion properties of the materials. Thus, due to the conducted study the most efficient content of the phthalic acid anhydride as a modifier has been determined to form the coatings of functional purpose.

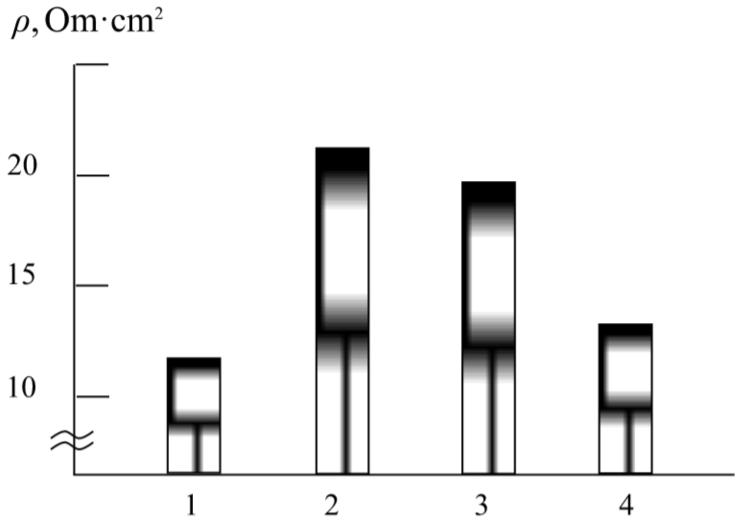

Figure 4. Values of specific resistance of protective coatings at frequency 1 kHz in aggressive environment of river water depending on the modifier PAA content, *q*, pts.wt.:1 – epoxy matrix (test sample); 2–1,0; 3–1,5; 4–2,0

Conclusions. Some innovative technologies have been applied in the paper under discussion dealing with the development of corrosion-resistant coatings aimed at ship navigation equipment protection. They have provided the optimization of components in formation of coatings of functional use according to the following criteria: adhesive strength, residual stresses and corrosion resistance.

According to the results of the study of composites adhesive properties depending on the phthalic acid anhydride as a modifier content we can state the following. To form a composite material or a protective coating with advanced adhesive properties and insignificant residual stresses one should apply the phthalic acid anhydride as a modifier to the epoxy matrix of amount q = 1,25 pts.wt. per q = 100 pts.wt. of epoxy matrix (oligomer ED-20 + plasticizer DEG-1). In this case, adhesive strength of the coating has increased from σ_a = 28,3 MPa to σ_a = 46,4 MPa, but residual stresses – from $\sigma_з$ = 1,9 MPa to $\sigma_з$ = 2,1 MPa. The improved properties of the modified materials are, first of all, the result of interaction of active carbonyl (C=O) groups of the modifier with nitrogen- containing (NH-) groups of the hardener. It has provided the higher degree of composites cross linking and, as a result, contributed to the advanced adhesive and cohesive properties in complex.

Moreover, we have found that the modifier application to the compound of content q = 1,0…1,5 pts.wt. per 100 pts.wt. of the matrix has provided an increase of resistance of the coatings under river water conditions from ρ = 12,1 Om·cm^2 to ρ = 21,2…22,4 Om·cm^2. Any further increase of the additive content in the coating has resulted in some deterioration of anti-corrosion properties of the materials. Thus, due to the conducted study the most efficient content of the phthalic acid anhydride as a modifier has been determined to form the coatings of functional purpose.

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ІННОВАЦІЙНІ ТЕХНОЛОГІЇ ПРИ РОЗРОБЛЕННІ КОРОЗІЙНОСТІЙКИХ ПОКРИТТІВ ДЛЯ ЗАХИСТУ ТЕХНІЧНИХ ЗАСОБІВ СУДНОВОДІННЯ

Олег Безбах

Херсонська державна морська академія, Херсон, Україна

Резюме. *Обґрунтовано перспективність застосування з метою підвищення антикорозійних властивостей засобів транспорту інноваційних технологій при створенні адгезивів із підвищеними експлуатаційними характеристиками. Такі технології передбачають застосування у складі покриттів активних до взаємодії інгредієнтів, які при зшиванні покриттів, у тому числі й полімерів, забезпечують суттєве поліпшення їх когезійних властивостей. Як основний компонент для зв'язувача при формуванні композитів вибрано епоксидний діановий олігомер марки ЕД-16. Додатково до епоксидного олігомера вводили пластифікатор у вигляді аліфатичної смоли ДЕГ-1 (ГОСТ 10136-77). Компаунд формували за наступної концентрації: епоксидна смола ЕД-16 : пластифікатор ДЕГ-1 – 100 : 40. При полімеризації розроблених матеріалів на основі епоксидної смоли застосовували твердник холодного тверднення поліетиленполіамін ПЕПА (ТУ 6-05-241-202-78). У вигляді модифікатора для поліпшення властивостей епоксидних композитних матеріалів використано фталевий ангідрид. Модифікатор вводили у зв'язувач за вмісту від 0,10 до 2,00 мас.ч. на 100 мас.ч. епоксидного олігомера ЕД-20. Молекулярна формула* *модифікатора: $C_8H_4O_3$. Молярна маса – 148,1 г/моль. Густина – ρ = 1,52 г/см³. Для формування композитного матеріалу чи захисного покриття з поліпшеними адгезійними властивостями та незначними залишковими напруженнями у епоксидний зв'язувач доцільно вводити модифікатор фталевий ангідрид у кількості q = 1,25 мас.ч. на q = 100 мас.ч. епоксидного зв'язувача (олігомер ЕД-20 + пластифікатор ДЕГ-1). При цьому адгезійна міцність покриття зростає від σ_a = 28,3 МПа до σ_a = 46,4 МПа, а залишкові напруження – від $\sigma_з$ = 1,9 МПа до $\sigma_з$ = 2,1 МПа. Покращення властивостей модифікованих матеріалів, у першу чергу, зумовлено взаємодією активних карбонільних (С=О) груп модифікатора з азотовмісними (NH-) групами твердника. Це забезпечує підвищення ступеня зшивання композитів, що, у свою чергу, призводить до підвищення показників їх як адгезійних та когезійних властивостей. Додатково встановлено, що введення у компаунд модифікатора за вмісту q = 1,0…1,5 мас.ч. на 100 мас.ч. зв'язувача забезпечує підвищення опору витриманих у річковій воді покриттів від ρ = 12,1 Ом·см^2 до ρ = 21,2…22,4 Ом·см^2. Надалі збільшення вмісту добавки у покритті призводить до погіршення антикорозійних властивостей матеріалів. Отже, на основі проведених досліджень встановлено оптимальний вміст модифікатора фталевого ангідриду для формування покриттів функціонального призначення.*

Ключові слова: *композит, адгезив, корозія, покриття, інноваційні технології.*

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