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INCREASING THE RELIABILITY OF NAVIGATION TOOLS UNDER THE INFLUENCE OF VARIABLE TEMPERATURES FOR EFFICIENT OPERATION BY WATER TRANSPORT

Introduction

Means of navigation ensure the safety and efficiency of the movement of vessels during the transportation of various cargoes by waterways. In particular, this applies to the transportation of energy resources (gas, oil, oil products), which are necessary to ensure the reliable operation of industrial enterprises and the needs of society. The means of navigation include equipment (antennas, echo sounders, radars, compasses) and systems (identification systems, dynamic positioning, radio and satellite communication, etc.) designed for navigation at sea and effective control of the vessel during operation.

Statement of Problem

For the reliable operation of navigation aids, it is necessary to monitor the condition of their external surfaces, in particular, the resistance of the paint coating to the influence of an external aggressive environment (the presence of signs of corrosion, mechanical damage, wear of protective coatings) by the requirements of the International Maritime Organization (IMO), taking into account resolution A.744 (18) [1, 2] and the International Convention for the Safety of Life at Sea (SOLAS, Chapters IV, V), taking into account resolution MSC.215(82) [3, 4]. According to the rules of the classification societies (DNV, Lloyd's Register), the condition of the navigation equipment, including the condition of the paint coating, is checked during the annual inspection of the ship [5]. If defects in the form of corrosion, cracks, or paint damage are detected, they must be replaced (reviews every 5 years). In addition, according to the International Association of Maritime Navigation and Lighthouse Services (IALA, section 6.2.1.2–6.2.1.4), paint coatings should not contain lead, tributyltin, tributyltin, and other harmful additives. Considering the above, there is a need to find new ingredients for creating protective coatings for the navigation complex, which will consider the requirements of international organizations, classification societies, associations, and conventions.

Analysis of the Latest Studies and Publications

To solve the problem of protection from external aggressive factors (moisture, seawater, ultraviolet radiation, temperature changes) of ship metal structures and equipment, particularly the navigation complex, high-quality polymer coatings are used [6–8]. This is the primary effective and efficient way to ensure the reliable operation of navigation technical means of water transport. Quite significant fire protection of carbon steel Q235 (St3kp), from which the working surfaces of navigation aids are made, was created by the authors of the work [9]. Filling the E-44 epoxy binder with zinc particles (5–15 μm) and three-dimensional graphene (3DG) (transverse size 10–50 μm, thickness 3–8 nm) allows to increase the corrosion resistance of polymer coatings that were studied in laboratory conditions. They are simulating a seawater environment using a 3,5 % NaCl solution. The use of biocidal additives in forming protective coatings is no less compelling. So, for example, the introduction of oxytetracycline at a content of q = 0,5 pts.wt. in epoxy oligomer DER – 331 (100 pts.wt.) allows to obtain protective coatings with a complex of improved properties (adhesive strength, physical-mechanical and thermophysical properties). In addition, the polymer coating based on oxytetracycline has an inhibitory effect on probiotic strains of Lactobacillus acidophilus, Bifidobacterium bifidum, Escherichia coli [10], as a

1.3-2.5-fold decrease in CFU/ml of test strains is observed in aggressive environments. Therefore, using similar biocides to protect means of navigation is relevant.

The aim of the work aims to study the effect of biocidal filler on the thermophysical characteristics of epoxy protective coatings designed to protect the surfaces of navigation aids.

Materials and Investigation Procedure

The following ingredients were selected for the creation of polymer coatings designed to protect the surfaces of metal structures, in particular, the surfaces of navigation equipment: binder – epoxy oligomer ED-20 (ISO 18280:2010); hardener – polyethylene polyamine (PEPA) (TU 6-05-241-202-78), according to the ratio of components (pts.wt.) – ED-20 : PEPA – 100 : 10. To improve the properties, the biocidal filler trimethoprim $C_{14}H_{18}N_4O_3$ (CAS: 738-70-5), which is a synthetic antibiotic capable of inhibit microorganisms and bacteria.

The technology of coating formation was carried out in a specific sequence specified in works [10–13].

Research on thermal resistance was carried out using thermogravimetric (THA) and differential thermal (DTA) analysis, using the «Thermoscan-2» derivatograph [11].

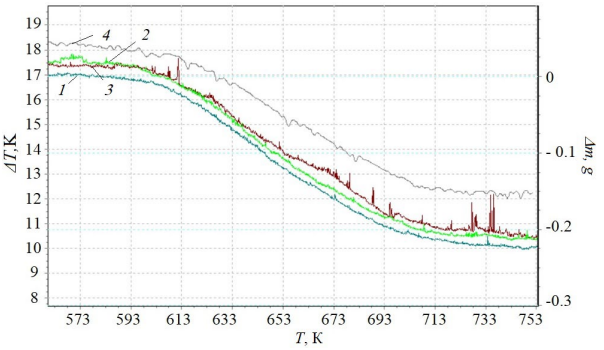
The activation energy was calculated by mathematical processing of the TGA curve according to Broido's method [12].

IR spectra were obtained using an "IRAffinity-1" spectrophotometer in the range of wave numbers $\nu = 400–4000$ cm^{-1}, according to work [11].

Results and Discussion

During the operation of navigation aids, the working elements are located in open areas, which are exposed to various external aggressive factors (changing temperatures, humidity, seawater, and ultraviolet radiation). Thus, it is advisable to analyze the influence of each of the specified factors on the characteristics of the developed coatings. Previously, the work focused on the analysis of the impact of the content of the biocidal filler trimethoprim ($C_{14}H_{18}N_4O_3$) in the epoxy binder on the thermophysical properties of protective coatings. Determining the rational content of the filler will allow the previous stage to improve the thermophysical indicators of protective coatings and, at the next stage – test the developed coatings compositions for anti-corrosion characteristics in a salt fog environment and resistance to ultraviolet radiation.

Thermophysical characteristics of protective coatings with different trimethoprim content were studied by thermogravimetric (TGA) and differential thermal (DTA) analysis. Previously, thermogravimetric analysis of epoxy composites with different contents of trimethoprim (5.0–30.0 pts.wt.) was performed in the temperature range $\Delta T = 303$-753 K. TGA analysis allows us to determine the beginning of structural transformations in CM under the influence of temperature. It is shown (Fig. 1, Table 1) that the lowest initial temperature of mass loss is characterized by the epoxy matrix – $T_0 = 587$ K.



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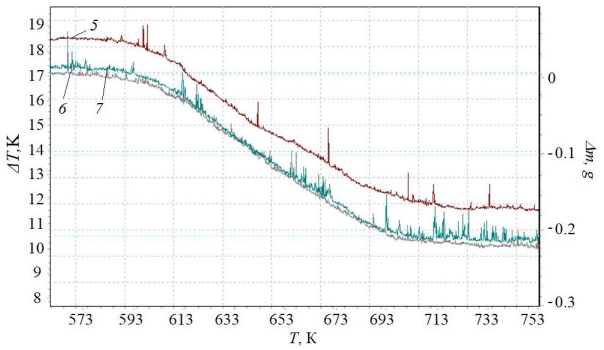

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Fig. 1. Results of thermogravimetric analysis of composites filled with $C_{14}H_{18}N_4O_3$:
1 – matrix (without filler); *2* – 5.0 pts.wt.; *3* – 10.0 pts.wt.; *4* – 15.0 pts.wt.; *5* – 20.0 pts.wt.; *6* – 25.0 pts.wt.; *7* – 30.0 pts.wt.

It was believed that this is connected with the beginning of the degradation of methylene -CH_2- groups in the structural network of the polymer. Then, the introduction of trimethoprim (10.0–15.0 pts.wt.) allows for a partial increase in the initial temperature of mass loss – $T_0 = 590–609$ K, which is associated with the effect of the additive on the mobility and deformability of methylene -CH_2- groups. At temperatures <600 K, intensive mass loss of filled polymers was observed. At the same time, for epoxy composite coatings filled with 10.0–15.0 pts.wt. $C_{14}H_{18}N_4O_3$ observed a change in the mass of the polymer ($T_{5\text{-}20}$ %) at higher temperatures (Table 1).

Table 1

Thermogravimetric analysis of polymeric materials

Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.	T_0, K	T_5, K	T_{10}, K	T_{20}, K	T_f, K	ε_m, %
0	587	616	625	641	714	80
5,0	590	617	633	646	733	73
10,0	609	620	637	648	738	68
15,0	609	624	640	652	740	69
20,0	600	620	630	642	734	69
25,0	600	620	631	642	727	58
30,0	602	621	634	640	727	54

This indicates the influence of the dispersed filler on the mobility of segments of the polymer network and the main chain of the epoxy polymer. For such composites, in the process of thermal tests, a slight change in mass (compared to the studied CMs) was established with increasing temperature – ε_m = 67–69 %. At the same time, the lowest value of the relative mass loss – ε_m = 54 %, was established for CM with the maximum content of $C_{14}H_{18}N_4O_3$, which is 25,0–30,0 pts.wt. Looking at the previous research results [12] and the results of TGA and DTA curves, it can be stated that this effect is related to the maximum filling of the polymer, where the change in the mass of the polymer is associated with the process of destruction of the filler itself (the content of which is maximum).

In addition, mathematical methods for determining thermal effects, particularly the activation energy of thermal destruction, were used to determine the stability of the developed epoxy composite coatings under the influence of elevated temperatures. Considering kinetic data at various stages of thermal oxidative destruction, the iso conversion method allows you to determine the activation energy of thermal destruction of polymer coatings, regardless of the degree of conversion. The method collects data at different heating rates, which allows for calculating the activation energy (E_a, kJ/mol) for different conversion levels. This method determines the temperature at which a certain degree of conversion α (5 %, 10 %, 20 %) is achieved at different heating rates. Among isoconversion methods, the most famous are [15–17]: Friedman's method, where it is possible to calculate E_a through derivatives, which requires accuracy in experimental data; Flynn-Wall-Ozawa (FWO), where the Arrhenius equation is used, which allows you to avoid derivatives, as well as experimental errors; the Kissinger-Akahira-Sunose (KAS) method, by plotting ln (β/T^2) versus 1/T; Starink methods, which is one of the improved methods, allows you to avoid exact knowledge of the kinetic model of the reaction and is based on the Arrhenius equation. Regardless of the advantages and disadvantages of the methods as mentioned earlier, when calculating the activation energy of thermal destruction, the advantage was given to the Broido method, which involves the graphical determination of E_a, through the display of the tangent of the slope angle (tg(φ)) of the logarithmic dependence of Δm on the inverse temperature T. [14].

Thus, the activation energy of thermal destruction for epoxy composite coatings with different $C_{14}H_{18}N_4O_3$ filler content was determined using TGA curves (Fig. 2).

Considering structural transformations (Table 1), the temperature range for mathematical calculations was assumed to equal – ΔT = 573–713 K. The mass loss for the investigated epoxy composite coatings was determined with an interval of ΔT = 10 K (Table 2, 3). At the same time, fig. 2 graphically displays the change in the mass of the studied epoxy composite coating filled with $C_{14}H_{18}N_4O_3$ with a content of 15.0 pts.wt. with a step of ΔT = 20 K (to understand the process of determining mass loss according to TGA curves). Similar mathematical calculations were performed for all investigated epoxy composite coatings (Table 2, 3).

According to Broido's method, the mass loss of the studied epoxy composite coatings was calculated as a percentage (Table 2, 3) using formula 1. The mass of the composite material at the initial temperature was taken as 100 %.

$$(100 - \Delta m)\% = \left(100 - \left(\frac{m_{in} + \Delta m}{\Delta m} \cdot 100\right)\right)\%, \quad (1)$$

where m_{in} – sample mass at the temperature (T_1 = 573 K = const); Δm – mass of the polymer as the temperature increases.

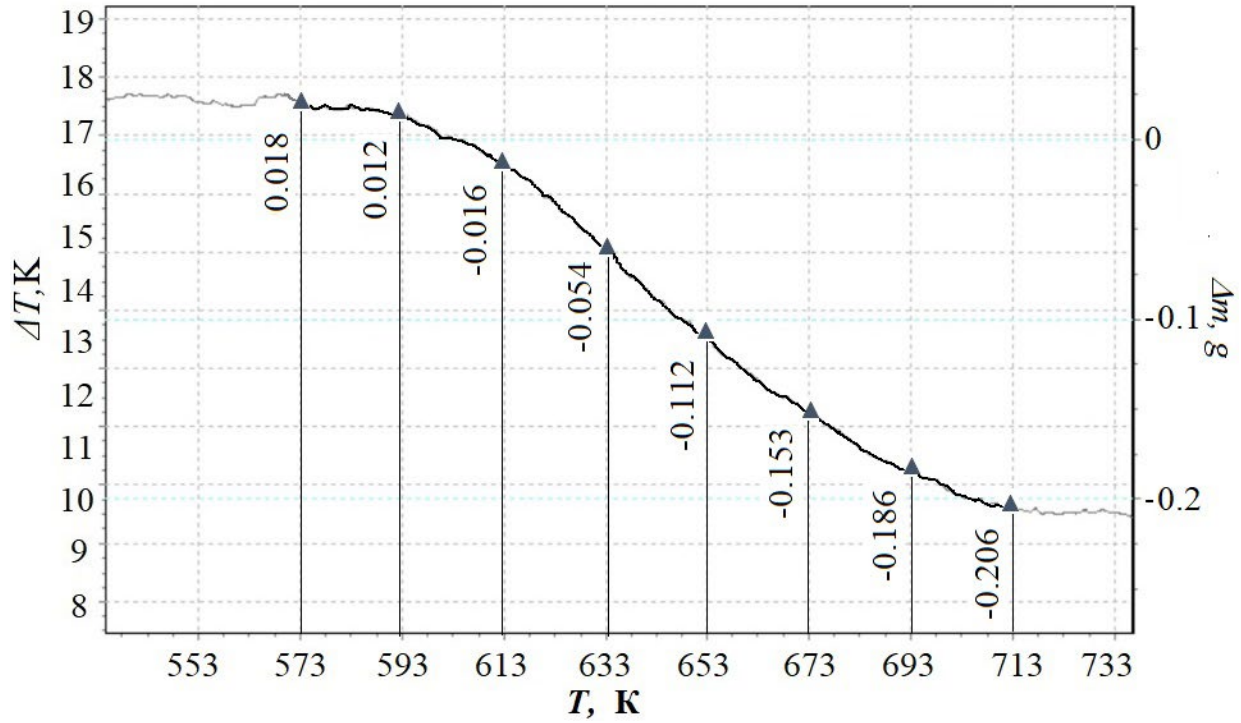


Fig. 2. Loss of mass of the epoxy composite coating filled with $C_{14}H_{18}N_4O_3$ (at a content of 15.0 pts.wt.) at ΔT = 573–713 K

Table 2

The value of the change in the mass of the studied materials, according to the TGA curve (1)

T, K	Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.							
	0		5,0		10,0		15,0	
	g	(100-Δ*m*), mg %	g	(100-Δ*m*), mg %	g	(100-Δ*m*), mg %	g	(100-Δ*m*), mg %
573	-0,005	1,42	0,002	-0,67	0,014	-4,83	0,018	-6,21
583	-0,007	1,99	-0,001	0,33	0,014	-4,83	0,017	-5,86
593	-0,009	2,56	-0,004	1,33	0,012	-4,14	0,012	-4,14
603	-0,021	5,97	-0,010	3,33	0,001	-0,34	-0,001	0,34
613	-0,044	12,50	-0,024	8,00	-0,015	5,17	-0,016	5,52
623	-0,052	14,77	-0,047	15,67	-0,031	10,69	-0,036	12,41
633	-0,069	19,60	-0,071	23,67	-0,060	20,69	-0,054	18,62
643	-0,094	26,70	-0,096	32,00	-0,086	29,66	-0,062	21,38
653	-0,110	31,25	-0,120	40,00	-0,105	36,21	-0,112	38,62
663	-0,128	36,36	-0,142	47,33	-0,117	40,34	-0,134	46,21
673	-0,134	38,07	-0,161	53,67	-0,137	47,24	-0,153	52,76
683	-0,147	41,76	-0,180	60,00	-0,159	54,83	-0,173	59,66
693	-0,159	45,17	-0,198	66,00	-0,182	62,76	-0,186	64,14
703	-0,167	47,44	-0,206	68,67	-0,191	65,86	-0,200	68,97
713	-0,179	50,85	-0,215	71,67	-0,201	69,31	-0,206	71,03

The mass loss of the studied material is characterized by a process of the first kind ($n = 1$), with a linear dependence of ln (100/(100 – Δ*m*) on the inverse temperature $10^3/T$, K^{-1}. At the same time, having determined the change in the mass of the composite (Δm) at temperature *T*, it is possible to graphically construct a line where E_a is represented by the tangent of the slope angle (tg(φ)) of the logarithmic dependence Δm on the inverse temperature *T*. This makes it possible to determine the value of the activation energy of thermo-oxidative destruction (kJ/mol) according to the formula:

$$E_a = -R \cdot \mathrm{tg}(\varphi). \qquad (2)$$

Table 3

The value of the change in the mass of the studied materials, according to the TGA curve (2)

T, K	Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.					
	20.0		25.0		30.0	
	g	(100-Δ*m*), mg %	g	(100-Δ*m*), mg %	*g*	(100-Δ*m*), mg %
573	-0,002	0,69	0,007	-2,19	0,043	-13,44
583	-0,003	1,03	0,006	-1,88	0,043	-13,44
593	-0,007	2,41	0,002	-0,63	0,039	-12,19
603	-0,014	4,83	-0,006	1,88	0,027	-8,44
613	-0,030	10,34	-0,024	7,50	0,014	-4,38
623	-0,050	17,24	-0,045	14,06	-0,012	3,75
633	-0,073	25,17	-0,070	21,88	-0,037	11,56
643	-0,095	32,76	-0,093	29,06	-0,062	19,38
653	-0,118	40,69	-0,113	35,31	-0,078	24,38
663	-0,138	47,59	-0,132	41,25	-0,090	28,13
673	-0,156	53,79	-0,151	47,19	-0,109	34,06
683	-0,174	60,00	-0,165	51,56	-0,128	40,00
693	-0,190	65,52	-0,169	52,81	-0,143	44,69
703	-0,203	70,00	-0,187	58,44	-0,151	47,19
713	-0,207	71,38	-0,197	61,56	-0,160	50,00

Table 4 presents the parameters used to calculate the activation energy of thermal destruction of epoxy composite coatings filled with $C_{14}H_{18}N_4O_3$.

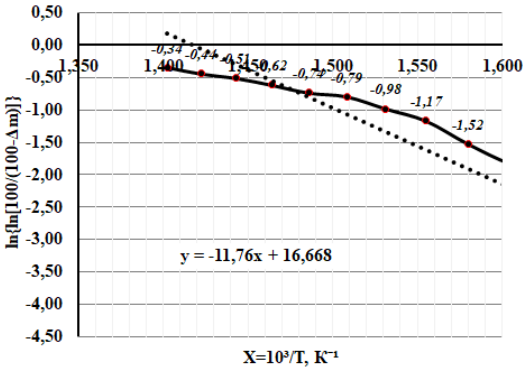
Table 4

Calculated values of the logarithm of the change in mass of epoxy composite coatings

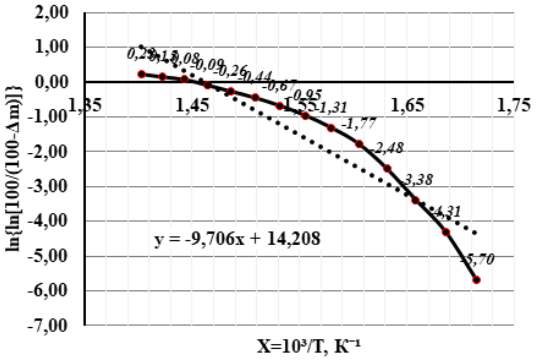
T, K	$10^3/T$, K^{-1}	ln{ln[100/(100-Δ*m*)]}						
		Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.						
		0	5,0	10,0	15,0	20,0	25,0	30,0
573	1,745	-4,24	–	–	–	-4,97	–	–
583	1,715	-3,90	-5,70	–	–	-4,56	–	–
593	1,686	-3,65	-4,31	–	–	-3,71	–	–
603	1,658	-2,78	-3,38	–	-5,66	-3,00	-3,96	–
613	1,631	-2,01	-2,48	-2,93	-2,86	-2,21	-2,55	–
623	1,605	-1,83	-1,77	-2,18	-2,02	-1,66	-1,88	-3,26
633	1,580	-1,52	-1,30	-1,46	-1,58	-1,23	-1,39	-2,09
643	1,555	-1,16	-0,95	-1,04	-1,42	-0,92	-1,06	-1,53
653	1,531	-0,98	-0,67	-0,80	-0,71	-0,64	-0,83	-1,27
663	1,508	-0,79	-0,44	-0,66	-0,47	-0,43	-0,63	-1,10
673	1,486	-0,73	-0,26	-0,44	-0,28	-0,25	-0,44	-0,87
683	1,464	-0,61	-0,08	-0,23	-0,09	-0,08	-0,32	-0,67
693	1,443	-0,50	0,07	-0,01	0,02	0,06	-0,28	-0,52
703	1,422	-0,44	0,14	0,07	0,15	0,18	-0,13	-0,44
713	1,403	-0,34	0,23	0,16	0,21	0,22	-0,04	-0,36

A straight line was graphically displayed to determine the activation energy, and the tangent of the angle of inclination φ was determined (Fig. 3. a-j, formula 3). This made it possible to mathematically determine the thermal effect through the activation energy of thermal destruction (formula 2).

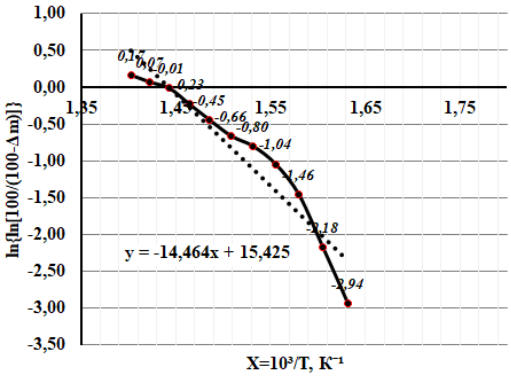
$$- \mathrm{tg}(\varphi) = y_i/x_i, \quad (3)$$



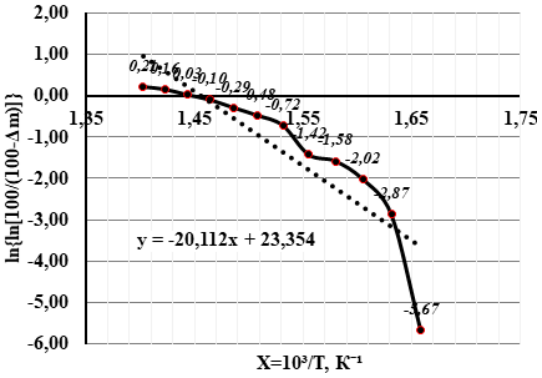
a – $tq_{(\varphi)}$ = 11,76



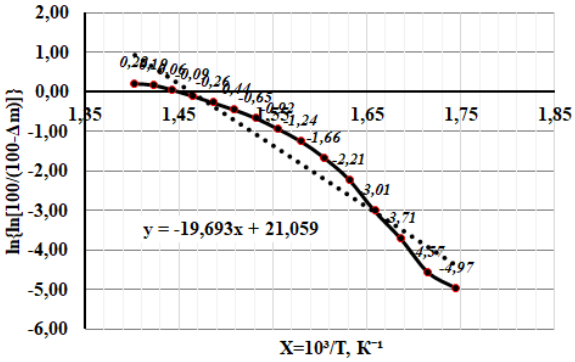
b – $tq_{(\varphi)}$ = 9,70



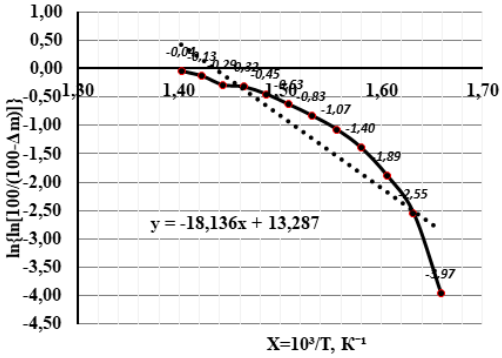
c – $tq_{(\varphi)}$ = 14,46



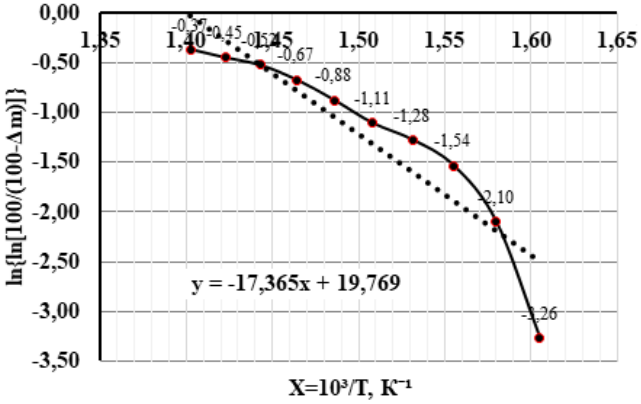
d – $tq_{(\varphi)}$ = 20,11



e – $tq_{(\varphi)}$ = 1969



f – $tq_{(\varphi)}$ = 18,13



j – $tq_{(\varphi)}$ = 17,36

Fig. 3. Logarithmic dependence of Δm on the reverse temperature of 10^3/T during thermal destruction of epoxy composite coatings: *a* – matrix (without filler); *b* – 5,0 pts.wt.; *c* – 10,0 pts.wt.; *d* – 15,0 pts.wt.; *e* – 20,0 pts.wt.; *f* – 25,0 pts.wt.; *j* – 30,0 pts.wt.

Based on mathematical calculations, the analytical results of the graphic determination of the activation energy of the developed materials are given (Table 5). The obtained results show that the activation energy increases curvilinearly with an increase in the content of $C_{14}H_{18}N_4O_3$ in the polymer coating.

The curvilinear dependence indicates the structural heterogeneity of the polymer, which affects the degradation of the epoxy binder and, accordingly, the processes of thermal destruction. It was believed that an increase in activation energy indicates a decrease in the speed of the thermo-oxidative destruction of epoxy composite coatings. At the same time, it was noted that for the thermal decomposition of the epoxy composite filled with dispersed $C_{14}H_{18}N_4O_3$ with a content of 15,0 pts.wt., the highest activation energy (167 kJ/mol) of all the considered materials (Table 5) is required, which indicates the stability of physico-chemical connections to the influence of elevated temperature.

Table 5

The activation energy of thermal destruction of epoxy composite coatings filled with dispersed $C_{14}H_{18}N_4O_3$

Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.	X_{HD}	X_k	X_i	Y_H	Y_k	Y_i	$tq_{(\varphi)}$	Energy Activation E_a, *kJ*/mol
Matrix	1,745	1,403	0,342	-17,740	-16,668	4,022	11,74	97
5,0	1,686	1,403	0,283	-9,706	-14,208	2,747	9,70	80
10,0	1,631	1,403	0,228	-14,464	-15,425	3,298	14,46	120
15,0	1,658	1,403	0,255	-20,112	23,354	5,129	20,11	167
20,0	1,745	1,403	0,342	-19,693	21,059	6,735	19,69	163
25,0	1,658	1,403	0,255	-18,136	13,287	4,625	18,13	150
30,0	1,050	1,403	0,202	-17,365	19,769	3,508	17,36	144

Structural changes that occur with a uniform temperature increase were studied using the differential thermal analysis method. Based on the analysis of DTA curves (Fig. 4, Table 6), it was established that composites filled with dispersed particles of trimethoprim with a content of 15,0 pts.wt. are characterized by the maximum value of the initial temperature of the exoeffect – T_{init} = 488 K. In this way, it is possible to ascertain the ability of the filler to inhibit the process of thermal destruction, due to the physical and chemical interaction of a significant number of bonds of the polymer with the biocidal additive. When comparing the curve of DTA and TGA, it can be stated that at the initial temperature of the exoeffect, there is no mass loss of the studied materials. A similar effect indicates the initial stage of thermal oxidation of the polymer, which is consistent with works [18–21]. Additionally, it was established that the maximum value of the peak of the exoeffect also shifts (relative to the unfilled polymer matrix) to the region of higher temperatures. The obtained data allow us to state that introducing $C_{14}H_{18}N_4O_3$ dispersed particles into the polymer matrix slows down the process of thermal destruction. Using such materials to protect the means of navigation during operation in conditions of variable temperatures is advisable. However, the TGA and DTA analysis results are insufficient to clarify the permissible temperature range at which it is possible to use the developed epoxy composite coatings (considering the climatic conditions of the ship's operation). Therefore, the analysis of structural changes that occur during heating in epoxy composite coatings was carried out with the additional involvement of the IR spectral analysis method. An epoxy composite coating was chosen for experimental studies, characterized by the maximum thermal stability parameters (T_0 = 609 K, E_a = = 167 kJ/mol, T_{init} = 488 K, T_{max} = 550 K). That is, this coating contains 15,0 pts.wt. dispersed filler trimethoprim ($C_{14}H_{18}N_4O_3$). IR spectra were registered in stages (initial polymer → polymer at T_{init} → polymer at T_{max}), in order of increasing temperature (Fig. 5).

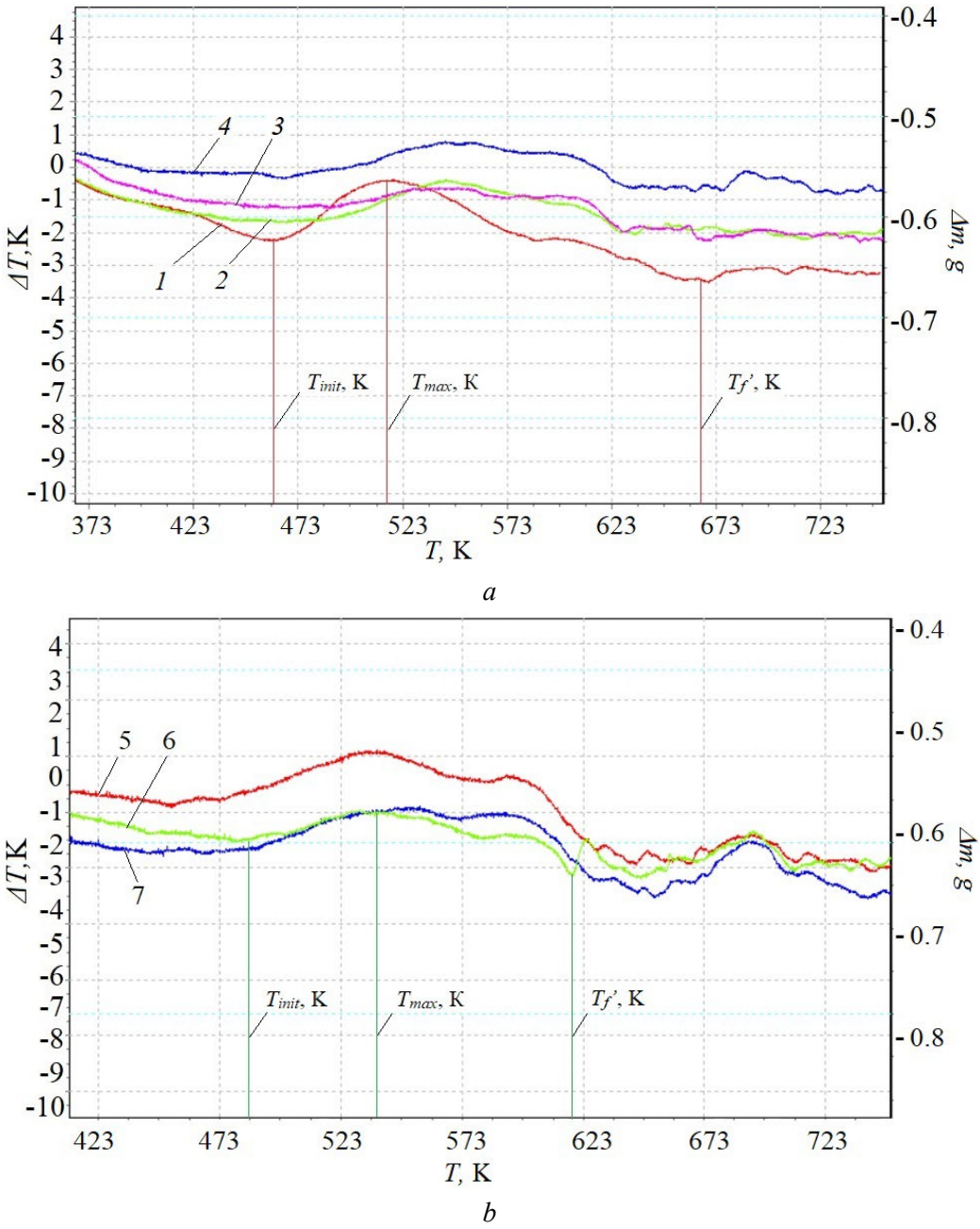


Fig. 4. Results of differential thermal analysis of composites filled with $C_{14}H_{18}N_4O_3$:
1 – matrix (without filler); *2* – 5,0 pts.wt.; *3* – 10,0 pts.wt.; *4* – 15,0 pts.wt.; *5* – 20,0 pts.wt.;
6 – 25,0 pts.wt.; 7 – 30,0 pts.wt.

Table 6

Differential thermal analysis of polymeric materials

Content of a $C_{14}H_{18}N_4O_3$, q, pts.wt.	Temperature Intervals of Exoeffects				Maximal Temperature Exoeffects, T_{max}, K
	T_{init}, K	T_f', K	ΔT_1, K	ΔT_2, K	
Epoxy matrix	460	659	199	3,05	518
5,0	466	632	166	1,35	545
10,0	473	633	160	1,59	545
15,0	488	663	175	1,54	550
20,0	453	643	190	2,01	538
25,0	462	647	185	1,48	545
30,0	474	643	169	1,13	538

The IR spectrum of the experimental material (epoxy composite coating with 15,0 pts.wt. of $C_{14}H_{18}N_4O_3$), which was not heated (Fig. 5, spectrum 1), was previously obtained. At the same time, the following polymer groups were detected at wave numbers: ν = 597 cm^{-1} (methylene -CH_2 group); ν = 767 cm^{-1} (-NH-, -CH- pendulum oscillations); ν = 840 cm^{-1} (C-C- valence vibrations, primary amines: CH_2-NH_2, CH-NH_2); ν = 1246 cm^{-1} (valence vibrations of -C-N-, -C-O- groups, vibrations of epoxy C-O-C groups); ν = 1516 cm^{-1} (deformation vibrations of -NN- groups); ν = 1612 cm^{-1} (-NH_2 primary amines: -CH_2-NH_2); ν = 1886 cm^{-1} (oscillations of carbonyl C-O groups); ν = 2067 cm^{-1} (oscillations of isocyanate -N=C=O groups); ν = 2966 cm^{1} (-C-H- bonds in methylene groups); ν = 3456 cm^{-1} (valence vibrations of -OH- groups). In the future, the polymer was heated to the initial temperature of the exoeffect (T_{init}), and accordingly, the IR spectrum was recorded (Fig. 5, spectrum 2). Comparing the IR spectra of 1 (without the influence of temperature) and 2 (at a temperature of 488 K) revealed the absence of structural changes in the polymer. Only a slight change in transmission intensity was observed, which indicates the mobility of polymer macrochains and segments. Accordingly, the polymer was heated to the maximum exoeffect temperature (T_{max}) – 550 K, and the IR spectrum was recorded (Fig. 5, spectrum 3). In this case, significant structural changes were observed, namely the absence of almost all peaks (except for ν = 1049 cm^{-1}, which is responsible for epoxy groups C-O-C, C-O), which indicates the destruction of a significant number of the above bonds in the structural network of the polymer.

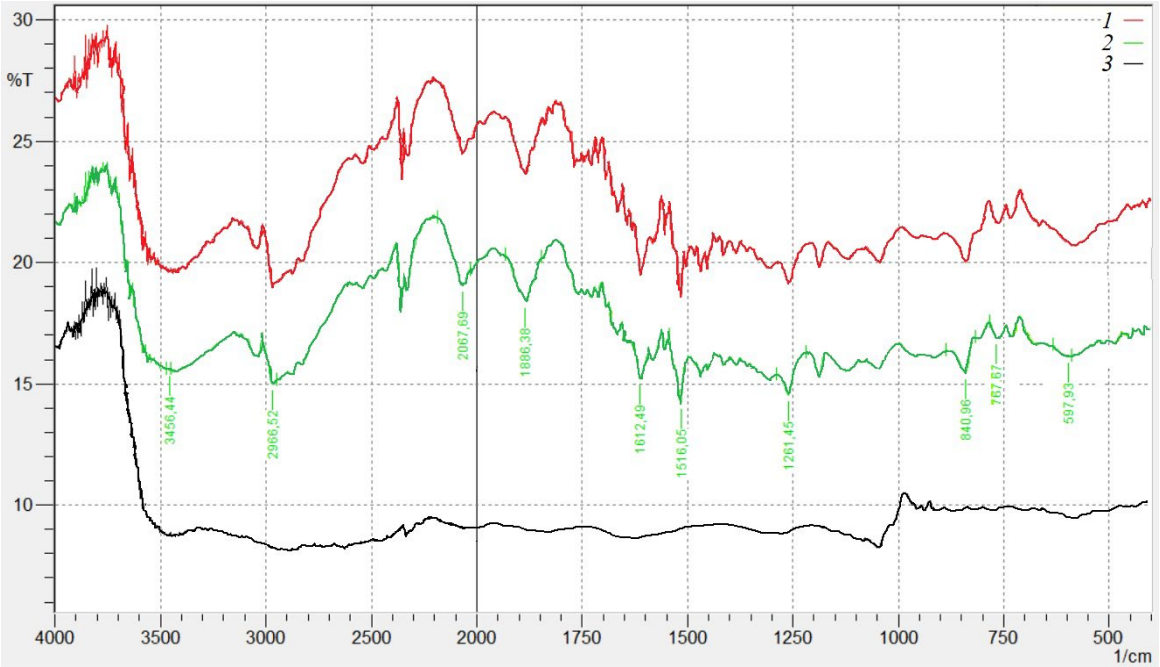


Fig. 5. IR spectral analysis of a polymer filled with dispersed $C_{14}H_{18}N_4O_3$ with a content of 15.0 pts.wt.: *1* – polymer material (spectrum) that was not exposed to temperature; *2* – polymer material (spectrum) at the beginning of the exoeffect; *3* – polymer material (spectrum) at the maximum value of the exoeffect

The work did not mention structural processes at the final temperature of the exoeffect (T_f') since the destruction of many chemical bonds was observed.

Conclusions

Based on the applied methods of DTA and TGA analysis, mathematical calculation of the activation energy of thermal destruction, and the method of IR spectral analysis, the structural processes that occur during heating of the developed epoxy composite coatings intended for the protection of the working surfaces of navigation means of water transport have been determined.

1. The TGA analysis proved that epoxy composite coatings filled with trimethoprim ($C_{14}H_{18}N_4O_3$) with a content of 15,0 pts.wt. are characterized by the highest initial mass loss temperature T_0 = 609 K. The shift of the initial temperature of mass loss to the region of high temperatures from T_0 = 587 K (for the epoxy matrix) to T_0 = 609 K (filled polymer) indicates the perception of heat energy by the dispersed additive and its redistribution in the volume of the epoxy composite coating due to the limitation of mobility and deformation of kinetic elements (segments and macrochains) of the polymer. This, in turn, indicates the thermal stability of the epoxy composite coating.

2. With the use of TGA curves and the performed mathematical calculation of the activation energy, it was proved that the maximum value of the excess thermal energy required for the destruction of chem-

ical bonds under the influence of variable temperature is characterized by epoxy composite coatings filled with trimethoprim ($C_{14}H_{18}N_4O_3$) at the above content. The activation energy is the largest among the investigated epoxy composite coatings and is E_a = 167 kJ/mol, 1,7 times greater than the unfilled polymer.

3. DTA analysis and IR spectroscopy were combined to clarify the structural processes with increasing temperature. Based on complex studies, it was established that the operating temperature of the developed epoxy composite coatings should not exceed 488 K. When the temperature exceeds 488 K, a significant number of bonds and polymer groups are destroyed, in particular: CH_2-, -NH-, -CH-, C-C -, CH_2-NH_2, CH-NH_2, C-O-C, -C-H-, -OH- and others. Therefore, exploiting the developed materials under the specified conditions is extremely limited and sometimes impossible.

At the following stages, the authors plan to test the developed epoxy composite coatings under exposure to ultraviolet radiation and in a salt fog environment.

REFERENCES

[1] ISO 9223. Corrosion of metals and alloys. Corrosivity of atmospheres. Classi®cation. ISO.Geneva. (1992). https://cdn.standards.iteh.ai/samples/16855/c18be4081cfc44aba101e3448e3539b6/ISO-9223-1992.pdf (access data 01.11.2024)

[2] International maritime organization IMO. RESOLUTION A.744(18) https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/AssemblyDocuments/A.744(18).pdf (access data 01.11.2024)

[3] SOLAS (Safety of Life at Sea) Consolidated Edition, 2020. https://www.samgongustofa.is/media/english/SOLAS-2020-Consolidated-Edition.pdf (access data 01.11.2024)

[4] RESOLUTION MSC.215(82). https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/MSCResolutions/MSC.215(82).pdf (access data 01.11.2024)

[5] Rules and Regulations for the Classification of Ships. https://www.imorules.com/LRSHIP.html (access data 01.11.2024)

[6] Lanruo Han, Qianyi Pang, Xiang Yu. Application of Organic Coating in Marine Anticorrosion. *Highlights in Science, Engineering and Technology*. 58, 131–141 (2023). https://doi.org/10.54097/hset.v58i.10051

[7] Wang N., Yin X., Zhang J., Gao H., Diao X., Yao H. Preparation and Anti-Corrosive Properties of Waterborne Epoxy Composite Coating Containing Graphene Oxide Grafted with Sodium Tripolyphosphate. *Coatings.* 10, 307 (2020). https://doi.org/10.3390/coatings10040307

[8] Alcántara J. Marine atmospheric corrosion of carbon steel: a review. *Materials.* 10 (4), 406 (2017). https://doi.org/10.3390/ma10040406

[9] DobrotvorI.G, Stukhlyak P. D., Mykytyshyn A. G., et al. Influence of Thickness and Dispersed Impurities on Residual Stresses in Epoxy Composite Coatings. *Strength Mater.* 53, 283–290 (2021). DOI:10.1007/s11223-021-00287-x

[10] Demchenko V. L., Kobylinskyi S. M., Riabov S. V., et al., Novel approach to the formation of silver-containing nanocomposites by thermochemical reduction of Ag+ ions in interpolyelectrolyte-metal complexes, *Appl. Nanoscience.* 10 (12), 5409–5419 (2020). DOI:10.1007/s13204-020-01368-0

[11] Stukhlyak P.D., Moroz K.M. Influence of porosity in the epoxy matrix-polyvinyl alcohol-disperse filler system on the impact toughness. *Mater. Sci.* 46(4), 455–463 (2011). https://doi.org/10.1007/s11003-011-9312-x

[12] Lazarenko M. M., Alekseev O. M., Kondratenko S. V., et al. Papadopoulos, Physical-chemical properties of nanocellulose synthesized from Miscanthus x Giganteus. *Mol. Cryst. Liq. Cryst.* 768 (1), 42–56 (2024). DOI:10.1080/15421406.2023.2231263

[13] Buketov A. V., Dolgov N. A., Sapronov A. A., Nigalatii V. D., Babich N. V. Mechanical Characteristics of Epoxy Nanocomposite Coatings with Ultradisperse Diamond Particles. *Strength of Materials.* 49 (3), 464–471 (2017). DOI 10.1007/s11223-017-9888-y

[14] Louda P., Sharko A., StepanchikovD., Sharko A. Experimental and Theoretical Study of Plastic Deformation of Epoxy Coatings on Metal Substrates Using the Acoustic Emission Method. *Materials.* 15 (11), 3791 (2022). https://doi.org/10.3390/ma15113791

[15] Totosko O. V., Stukhlyak P. D., Mykytyshyn A. H., Levytskyi V. V. Investigation of electrospark hydraulic shock influence on adhesive-cohesion characteristics of epoxy coatings. *Funct. Mater.* 27 (4), 760–766 (2020). https://doi.org/10.15407/fm27.04.760.

[16] Dolgov N., Stukhlyak P., Totosko O., et al. Analytical stress analysis of the furan epoxy composite coatings subjected to tensile test. *Mech. of Adv. Mater. and Struct.* 2023 (2023). https://doi.org/10.1080/15376494.2023.2239811

[17] Qin Z., Su Y., Bai Y., Lu H., Peng T., Zhong H., Chen T., Du X. Improving the Corrosion Resistance of Zn-Rich Epoxy Coating with Three-Dimensional Porous Graphene. *Polymers.* 15(21):4302 (2023). https://doi.org/10.3390/polym15214302

[18] Panda A., Dyadyura K., Valíček J., et al. Ecotoxicity Study of New Composite Materials Based on Epoxy Matrix DER-331 Filled with Biocides Used for Industrial Applications. *Polymers,* 14(16):3275 (2022). https://doi.org/10.3390/polym14163275

[19] Buketov A., Maruschak P., Sapronov O., Brailo M., Leshchenko O., Bencheikh L., Menou A. Investigation of thermophysical properties of epoxy Nanocomposites. *Molecular Crystals and Liquid Crystals.* 628, 167–179 (2016). DOI:10.1080/15421406.2015.1137122

[20] Sapronov O., Buketov A., Kim B., Vorobiov P., Sapronova L. Increasing the Service Life of Marine Transport Using Heat-Resistant Polymer Nanocomposites. *Materials*. 17, 1503 (2024) doi.org/10.3390/ma17071503

[21] Sapronov O., Maruschak P., SotsenkoV., et al., Development and Use of New Polymer Adhesives for the Restoration of Marine Equipment Units, *J. Mar. Sci. Eng.* 8 (7) 527 (2020). DOI:https://doi.org/10.3390/jmse8070527

[22] Broido, A.: A simple sensitive graphical method of treating thermo gravimetric analyze data. *J. Polym. Sci.- Part A*. 7, 1761–1773 (1969). https://doi.org/10.1002/pol.1969.160071012

[23] Arshad, M. A., Maaroufi, A., Benavente, R., Pereña, J. M., & Pinto, G. Thermal degradation kinetics of insulating/conducting epoxy/Zn composites under nonisothermal conditions. *Polymer Composites.* 34(12), 2049–2060 (2013). DOI:10.1002/pc.22613

[24] M. Azeem Arshad1, A. Maaroufi, R. Benavente, G. Pinto. Kinetics of the Thermal Decomposition Mechanisms of Conducting and Non-conducting epoxy. *J. Mater. Environ. Sci.* 5 (5), 1342–1354 (2014). https://www.semanticscholar.org/paper/Kinetics-of-the-Thermal-Decomposition-Mechanisms-of-Arshad-Maroufi/869e27f1cfaf8fb9da5f90093fe582df5b215164

[25] Friedman H.L. Kinetics of Thermal Degradation of Char-Forming Plastics from Thermogravimetry. Application to a Phenolic Plastic. Journal of Polymer Science. 6 (1), 183–185 (1964). DOI:10.1002/polc.5070060121

[26] Sun, X.; Li, Z.; Das, O.; Hedenqvist, M. S. Superior flame retardancy and smoke suppression of epoxy resins with zinc ferrite@polyphosphazene nanocomposites. *Compos. Part A Appl. Sci. Manuf.* 167, 107417 (2023). DOI:10.1016/j.compositesa.2022.107417

[27] Yu B., Shi Y., Yuan B., Qiu S., Xing W., Hu W., Song L., Lo S., Hu Y. Enhanced thermal and flame retardant properties of flame-retardant-wrapped graphene/epoxy resin nanocomposites. *J. Mater. Chem. A*. 5, 8034–8044 (2015). https://doi.org/10.1039/C4TA06613H

[28] Brnardic, I.; Macan, J.; Ivankovic, H.; Ivankovic, M. Thermal degradation kinetics of epoxy/organically modified montmorillonite nanocomposites. *J. Appl. Polym. Sci.* 107, 1932–1938 (2008). DOI:10.1002/app.27230

[29] Sapronov O. O., Buketov A. V., Zinchenko D. O., Yatsyuk V. M. Features of structural processes in epoxy composites filled with silver carbonate on increase in temperature. *Composites: Mechanics, Computations, Applications. An International Journal*. 8(1), 47–65 (2017). DOI: 10.1615/CompMechComputApplIntJ.v8.i1.10.

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ПІДВИЩЕННЯ НАДІЙНОСТІ РОБОТИ ЗАСОБІВ НАВІГАЦІЇ В УМОВАХ ВПЛИВУ ЗМІННИХ ТЕМПЕРАТУР ДЛЯ ЕФЕКТИВНОЇ ЕКСПЛУАТАЦІЇ РУХОМ ВОДНОГО ТРАНСПОРТУ

Водний транспорт завдяки розвинутої логістиці здійснює перевезення не обмеженого обсягу різнорідних вантажів. Тому, водний транспорт є одним із найбільших світових перевізників. У першу чергу це обумовлено розгалуженою мережею портів і морських шляхів, що дозволяє транспортувати вантажі на великі відстані, в тому числі міжконтинентальні. Тому, забезпечення глобального зв'язку має вирішальне значення для постачання вантажів у чітко встановлені терміни.

У роботі наведено технологічні аспекти поліпшення теплофізичних характеристик епоксикомпозитних захисних покриттів для захисту засобів навігації водного транспорту, які працюють в умовах впливу змінних зовнішніх факторів. Для формування епоксикомпозитних захисних покриттів використано епоксидний зв'язувач ЕД-20, який полімеризували твердником поліетиленполіаміном ПЕПА у співвідношенні: епоксидний олігомер ЕД-20–100 мас.ч. твердник ПЕПА – 10 мас.ч. Для підвищення теплофізичних властивостей полімерних матеріалів використовували біоцидний наповнювач триметоприм $C_{14}H_{18}N_4O_3$ (CAS: 738-70-5), за вмісту 5,0…30,0 мас.ч. На основі термогравіметричного (ТГА) та диференційно-термічного (ДТА) аналізу встановлено значення ключових параметрів, необхідних для визначення діапазону температур, при яких можливо експлуатувати розроблені епоксикомпозитні покриття призначені для захистку засобів навігації без зміни їх властивостей, зокрема: максимальна температура початку втрати маси становить – T_0 = 609 К; відносна втрата маси – ε_m = 69 %; початкова температура екзоефекту – T_n = 488 К; максимальне значення температури піку екзоефекту – T_{max} = 550 К. Виконано математичний розрахунок значень енергії активації термічної деструкції для визначення стійкості до руйнування хімічних зв'язків при впливі температури. Доведено, максимальним значенням енергії активації, що становить E_a = 167 кДж/моль, характеризуються епоксикомпозитні покриття,

наповнені триметопримом за вмісту 15,0 мас.ч., що свідчить про термічну стійкість наповнених епоксикомпозитних покриттів. Методом ІЧ-спектрального аналізу встановлено перебіг фізико-хімічних процесів термічної деструкції епоксикомпозитних покриттів, наповнених триметоприм.

На основі комплексних досліджень, з використанням ДТА-, ТГА-, ІЧ-спектрального аналізу і виконаного математичного розрахунку енергії активації доведено, що температурний діапазон експлуатації розроблених епоксидних покриттів не повинен перевищувати 488 К.

Ключові слова: навігація; покриття; деструкція; енергія активації; ІЧ-спектр.

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INCREASING THE RELIABILITY OF NAVIGATION TOOLS UNDER THE INFLUENCE OF VARIABLE TEMPERATURES FOR EFFICIENT OPERATION BY WATER TRANSPORT

Thanks to advanced logistics, water transport transports an unlimited amount of various cargoes. Therefore, water transport is one of the world's largest carriers. First, this is due to the extensive network of ports and sea routes, which allows transporting goods over long distances, including intercontinental ones. Therefore, ensuring global connectivity is critical to delivering goods on time.

The work presents the technological aspects of improving the thermophysical characteristics of epoxy composite protective coatings to protect navigational means of water transport that operate under variable external factors. The polymerized ED-20 epoxy binder was used with PEPA polyethylene polyamine hardener to form epoxy composite protective coatings. The biocidal filler trimethoprim $C_{14}H_{18}N_4O_3$ (CAS: 738-70-5) was used to increase the thermophysical properties of polymeric materials, with a content of 5.0–30.0 pts.wt. Based on thermogravimetric (TGA) and differential thermal (DTA) analysis, the values of the critical parameters necessary to determine the temperature range at which it is possible to operate the developed epoxy composite coatings intended for the protection of navigation aids without changing their properties, in particular: the maximum temperature of the beginning of mass loss is – T_0 = 609 K; relative mass loss – ε_m = 69 %; the initial temperature of the exoeffect is T_{init} = 488 K; the maximum value of the peak temperature of the exoeffect is T_{max} = 550 K. A mathematical calculation of the values of the activation energy of thermal destruction was performed to determine the resistance to the destruction of chemical bonds under the influence of temperature. It has been proven that epoxy composite coatings filled with trimethoprim at a content of 15.0 pts.wt. are characterized by the maximum activation energy of E_a = 167 kJ/mol, which indicates the thermal stability of filled epoxy composite coatings. The course of physicochemical processes of thermal destruction of epoxy composite coatings filled with trimethoprim was determined by the method of IR spectral analysis.

Based on complex studies using DTA, TGA, IR spectral analysis, and mathematical calculation of the activation energy, it was proved that the operating temperature range of the developed epoxy coatings should not exceed 488 K.

Keywords: navigation; coverage; destruction; activation energy; IR spectrum.

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