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14

Nanostructured compositions based on polymeric paintwork materials and environmentally safe biocides

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Composite coatings containing iodine- and bromine-containing compounds as biocides have been obtained on the basis of industrial paintwork materials. A number of composite coatings containing biocides - Nitroxynil, Ioxynil and 2,5-dibrom-4-nitrophenol, have been analyzed using a modified technique for assessing biological activity and toxicity for determining the survival rate of *Artemia salina* crustaceans. It was found that the compositions on the basis of paintwork materials with Nitroxynil show the greatest bioactivity. AFM study of the surface morphology of the developed coatings showed that the introduction of biocides leads to coating structuring at the nanolevel, with the strength of nanostructured coatings on impact decreases by 2-3 times, however, these values are 2 times higher than those of the reference sample — an industrial copper-containing antifouling paint. The obtained results can be used for further development of environmentally safe protective and antifouling polymer coatings and paintwork materials.

Keywords: protective and antifouling paintwork materials, iodine- and bromine-containing biocides, atomic-force microscopy, morphology of composite coatings, surface roughness, impact strength.

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Introduction

Problem of biodeterioration (biocorrosion) and fouling of watercraft, hydrotechnical facilities, oil and gas pipelines is a challenging scientific, economical and environmental task. All materials used in high humidity and favorable temperature conditions are susceptible to biodeterioration [1]. Aquatic microorganisms, invertebrate animals and algae are referred to as hydrobionts. Fouling organisms — are those hydrobiont species that live on hard substrates [2]. They populate the surfaces of engineering facilities — ships, harbor facilities, pipelines, oil and gas platforms. The main types of fouling organisms are sessile organisms. They use various attachment mechanisms to solid substrates [2,3]. Fouling organisms attach to the facility surfaces and cause serious operational problems. Roughness of metal surfaces of ships is increased and contributes to resistance to motion. Thus, as a result of fouling, ships may lose up to 40−50% of rate of sailing inevitably causing excessive fuel consumption. In pipelines, fouling organisms may block pipe internals and, thus, degrade machine and equipment cooling causing in some cases equipment damage and even complete shutdown. Some hydrobionts attach to electric cables and may degrade insulation and damage metal ropes [1,2,4].

Multiple methods are available to control biocorrosion and fouling of underwater facilities. In addition to the simplest method — mechanical cleaning — the following methods are, for example, used: thermal, electric, ultrasound or radiological protection near facilities [5]. Various biocorrosion control methods such as chemical and physical are described in detail in [6].

Currently, the most widely used and easily available biodeterioration and fouling control method is the use of paintwork materials (PWM) containing toxic substances — biocide additives [3,6]. By leaching out into environment, biocides prevent sedimentation and/or attachment of fouling organisms.

In the past, in the 1950s−1960s, mercuric oxide, organoarsenic or copper compounds, which belong to hazard class I and II, accumulate in hydrobiont organisms and contaminate water areas with toxic compounds, were introduced in antifouling coatings as biocides. Due to high hazard level in production and application, and hazard to marine environment and inhabitants, mercury and arsenic were prohibited for use in ship paints in the late 1960s. From the 1970s, organostannic compounds, which kill fouling organisms, were used as biocides in coatings, but due to their high toxicity, they were prohibited for introduction in ship coatings and subsequent ship painting by the International Marine Environment Protection Organization in 2008 [7].

Currently for this purpose, copper compounds with concentrations from 25 to 50 mass.% are used, however, they also may be prohibited in the nearest future due to emerging environmental hazard. Therefore, an essential objective includes the search for environmentally friendly biocides and the development of protective, in particular antifouling biocide-based PWM.

In addition to polymer filming agent, biocide PWM always contain various types of biocides, toxins or poisons destructive to fouling organisms. Various oligomers and polymers of natural or synthetic origin are used as filming agents such as colophony, chlorinated polyvinyl chloride, vinylchloride copolymers, chlorinated rubbers, chlorinated polyethylene, polyisobutylene, epoxy oligomers, etc. [6].

Earlier, [7] offered to use iodine-and bromine-containing compounds synthesized at JSC NPO „Iodobrom" (Saki, Crimea) for production of antifouling coating based on rubber-containing filming compositions. With time, these biocides released from coatings prevented fouling organism sedimentation and decomposed in sea water into environmentally friendly neutral iodine- and bromine-containing compounds whose composition was close to that of sea water. Full-scale sea tests for coating performance have shown that they are not accumulated neither in marine flora and fauna nor in bottom sediments.

The purpose of the research was to produce composite coatings (CC) on the basis of industrial PWM with various composition and iodine-/bromine-containing biocides, study morphology of CC film surface by atomic-force microscopy (AFM) and determine the correlation between their structural and morphological characteristics and strength properties and biological activity.

1. Experimental

1.1. Materials

Biocides were synthesized according to procedures described in [8–10]. Structural formulas of synthesized iodine- and bromine-containing biocides are shown in Figure 1.

Nitroxynil (N) is a yellow crystalline powder, poorly water-soluble, very soluble in organic solvents, melting temperature is $t_m = 137^\circ$C. Nitroxynil applications include the use as pharmaceutical drugs because it affects oxidative phosphorylation processes in helminths. This is a toxic drug, though it is capable of biotransforming into inactive metabolites under the action of bacterial microflora which is

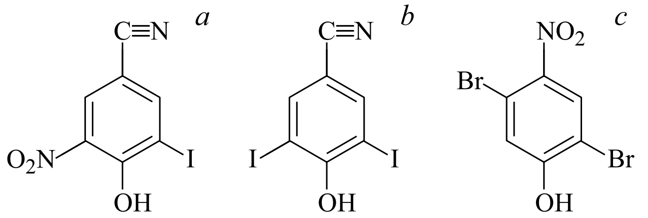

Figure 1. Structural formulas of synthesized biocides: *a* — nitroxynil (3-iodine-4-hydroxy-5-nitrobenzonitrile) (N), *b* — ioxynil (3,5-diiodo-4-hydroxibenzonitrile) (I), *c* — 2,5-dibromo-4-nitrophenol (P).

especially important for production of environmentally safe biologically active coatings.

Ioxynil (I) and 2,5-dibromo-4-nitrophenol (P) are used as active ingredients in various herbicide mixtures and pesticides. Ioxynil is a combustible photosensitive colorless solid substance with faint phenol odor which is virtually water-insoluble, $t_m = 112^\circ$C. 2,5-dibromo-4-nitrophenol is a solid substance, poorly water-soluble, $t_m = 144^\circ$C.

1.2. Preparation of biocide-containing compositions

Biocide compositions were obtained by means of biocide introduction into industrial PWM enamels constituting vinyl chloride-vinyl acetate copolymer (XC-720 enamel) and vinyl and epoxy resin copolymers (XC-436 enamel) in various concentrations. XC-720 enamel is a one-component material based on vinyl chloride-vinyl acetate copolymer. XC-720 enamel is intended for corrosion protection of underwater and above-water parts of ship. Coatings on its basis have high anticorrosion properties and ensure protection of metal in corrosive sea environment [11]. XC-436 enamel is a two-component material based on vinyl and epoxy resins. It is intended to ensure corrosion protection of underwater part of ship hulls (including ice-going ships) under the splash area, and anticorrosion protection of steel surfaces operated in ambient conditions.

Biocides were introduced in XC-436 and XC-720 enamels in various concentrations (1 to 20 mass.%). Test samples free of biocides and XC-5226 industrial antifouling copper-containing paint were also tested. XC-5226 enamel is a one-component material based on vinyl polymer modified with epoxy resin. The enamel is intended for antifouling protection of underwater ship hulls of unrestricted navigation ships [11].

Accurately weighed biocides (1 g) were solved in 10 ml of organic solvent mixture (P4). The obtained solutions (emulsions) were introduced in enamels and intensively mixed using mechanical mixer up to paint homogenization during 2 h. Vinyl polymer modified by epoxy resin (XC-5226 industrial antifouling paint containing 52 mass.% of cuprous oxide, colophony and aerosil). The prepared compositions were applied to glass surfaces of Petri dishes with brushes or steel plate, then dried in air at room temperature during 24 hours. To determine morphological characteristics, the obtained compositions were removed from the substrates by holding in formic acid, then films were rinsed in distilled water during 2 h, and dried at room temperature. After removal from the substrates, the films were not warmed.

1.3. Research methods

1.3.1. Biological tests of composite coating test samples

The most important parameter of toxin-containing PWM is their biological activity. For the purpose of this research, biocide and biocide-containing coating performance assessment procedure using biological activity against crustaceans [3,12].

Biological testing within this research used *Artemia salina* brackish-water crustaceans representative for assessment of antifouling properties of coating test samples [3]. *Artemia salina* crustacean eggs were placed in a vessel for nauplii (larvae) growing, compressor was connected and the vessel was filled with 5‰ salinated water. 5 g nauplii eggs were added per 1 litre. Eclosion was observed 24 hours after starting of the test system. Biological testing was carried out 2–3 days after nauplii eclosion.

10 ml of water with nauplii was added to Petri dishes with applied biocide-free coatings. Biological activity was assessed by the type of movement and survival rate of crustaceans. *Artemia salina* nauplii survival rate was assessed in percentage, survival rate was recorded at 30 min. interval.

Biological activity of biocide-containing coatings were studied in 2 replications for 3 biocides — N, I and P. Water with *Artemia salina* nauplii (50 ml) and biocide solution (1 ml) were added to Petri dishes. Time from the beginning of test substance exposure to full death based on absence of movement was the criterion for assessment of nauplii sensitivity to toxic substances. During several hours, viability of crustaceans was determined by their mobility and change in the type of motions. Based on the obtained data, mortality rate of larvae in coated dishes was calculated and compared with reference samples (sterile dishes). Nauplii condition was recorded 10, 30 and 60 min after solution introduction. Based on survival rate of crustaceans (and change in type of mobility) according to sensitivity to biocides introduced in coatings, coatings were ranked by their biological activity strength.

1.3.2. Determining theoretical biological activity using PASS Online software

Biological activity range (BAR) of a chemical compound is a set of various activities as a result of interaction between the compound and test organisms. BAR reflects the compound properties depending only on the compound structure and physicochemical characteristics. Publications and papers do not contain full description of BAR. PASS (Prediction of Activity Spectra for Substanses) software [13] is an instrument for biological potential forecasting of organic molecules. PASS forecasts various types of biological activity based on the structure of organic compounds because it contains information from various sources.

To forecast biological activity range of the compound using PASS Online, draw the compound structural formula in the built-in graphical editor. After results processing, the software generates a table listing various types of biological activities and evaluating the probability of each type for this compound. Probability of activity (Pa) or inactivity (Pi) of each compound is presented by numerical value from 0 to 1.

1.3.3. Determining strength properties of coatings exposed to impact

Strength of composite films exposed to impact was determined using „Konstanta U-1A"instrument designed for determining PWM coatings exposed to impact made by a method based on coated metal plate deformation after free load falling on the plate in accordance with GOST 4765-73 [14]. Load weight is 1 kg.

Biocide-containing compositions of two PWM types and biocides were applied to cold-rolled plates with magnesium-phosphate coating and left to dry for 24 hours. The plates were placed on the anvil under the striker with coating up. According to the instrument application procedure the plate area exposed to impact shall be at least 20 mm from the plate edges or from the centers of other areas previously exposed to impact. Load was lifted and fixed on a predefined height using a retaining screw. Then the load was released by pressing the pushbutton and the load fell on the striker. After the impact, the load was lifted, the plate was removed and the coating was examined for any cracks, coating removal or separation using a magnifying glass. If there were no defects, the test was repeated with increasing the load drop height by 20 mm until the film failure under impact was visually detected. The coating strength was assessed by maximum height at which 3 positive results (before the start of coating damage) were obtained.

Film impact strength was expressed by a maximum height number in cm from which the falling load did not cause any mechanical damage to the coating. The coating thickness on the plates was defined using micrometer. The average of 10 measurements was taken as the film thickness (in mm).

1.3.4 Determining structural-morphological characteristics of composite coatings

Morphological tests of the developed coatings were performed using Nanotop NT-206 atomic force microscope (ODO „Mikrotestmashiny", Belarus). Measurements were performed in contact mode under atmospheric conditions using silicon cantilevers NSC11/AlBS with stiffness coefficient $k = 3.0$ N/m and tip curve radius of 10 nm. Experimental data was processed using Surface Explorer software.

2. Results and discussion

Important benefits of biocide-containing PWM include simplicity, accessibility, ease of application (no expensive equipment is required), application in various climatic conditions. Disadvantages of biocide PWM include multiple layers, coating application time and environment pollution by toxic substances [6,15].

Table 1. *Artemia salina* (nauplii) death rate in biocide water solutions

№	Sample	Artemia salina nauplii death rate, %		
		10 min	30 min	60 min
1	Ioxynil	20	50	95
2	Nitroxynil	50	70	100
3	2,5-dibromo-4-nitrophenol	85	100	100
4	Reference sample (brackish water)	0	0	0

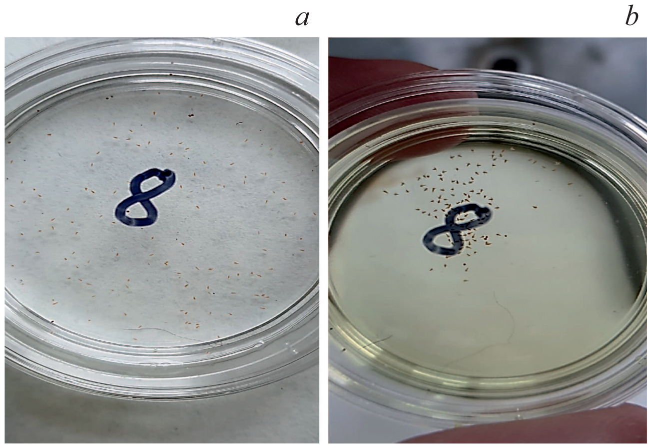

Figure 2. *Artemia salina* (nauplii) in the reference medium before the test (*a*) and in the test medium 30 min after introduction of biocide 2,5-dibromo-4-nitrophenol (P) (*b*).

2.1. Determining *Artemia salina* survival rate in biocide water solutions

Artemia eggs with high hatching percentage (about 100%) were used for the experiments. Table 1 shows the activity test results for three biocides — N, I and P in relation to two-day *Artemia salina* naulpii.

Figure 2 shows photos of Petri dishes with life crustaceans in brackish water (Figure 2, *a*, reference medium) and 30 min after introduction of 1 mass.% solution of the most active biocide — 2,5-dibromo-4-nitrophenol (Figure 2, *b*, test medium). It is evident that in the reference medium, crustaceans are evenly distributed throughout the water depth and are actively moving (Figure 2, *a*). After biocide P introduction into the test medium, nauplii accumulate at the water surface and completely lose their mobility in 30 min and their appearance is changed. Figure 2, *b* shows the dead nauplii organisms pre-concentrated in the upper quarter of the Petri dish by a directed light source (one- and two-day newborn nauplii have positive phototaxis). Nauplii death rate was 100% as early as 30 min after introduction of P. biocide solution. Nitroxyl and ioxyl showed lower activity (Table 1).

It should be noted that the synthesized biocides are low soluble in water. According to [2,6], low water solubility of biocides introduced in PWM is a necessary property for reduction of their washing out (leaching) from coatings.

2.2. Assessment of biological activity of composite coatings

Comparison of biological activity of three biocides — ioxynil, nitroxynil and 2,5-dibromo-4-nitrophenol was carried out by screening analysis of the number of dead crustaceans introduced in coated Petri dishes in two replications.

Table 2 contains the test results for XC-720 enamel coatings containing biocides using *Artemia salina*.

Review of the test results has shown that biocides I, N and P showed high activity — as early as in 10 min death of 50 to 85% *Artemia salina* was observed. Therefore, biocide concentration for biological testing of XC-436 enamel coatings was reduced to 1, 3 and 5 mass.%. Bioactivity test results of XC-436 enamel coatings using *Artemia salina* are shown in Table 3. Also, crustaceans survival rate was recorded 24 hours after the test start. Coating performance was calculated according to the survival rate results in 5 h.

Table 3 shows that the highest biological activity was shown by coating with nitroxylin (N). In a minimum concentration of 1%, the crustaceans death rate was equal to 60%. Performance of coatings with N within 1–5 mass.% is equal to 65–87%.

Coatings with ioxynil showed comparatively lower biological activity, performance is 18 – 45%. When comparing Tables 2 and 3 it is evident that coatings based on 5% enamels with various composition show different performance. Death rate of nauplii in biocide composition medium based on XC-720 enamel achieved 100% after 5 h, while for XC-436 enamel, this parameter was much lower — 40 to 80%. This may be caused by different biocide leaching rate from composite coatings with different composition.

2.3. Biological activity range forecasting in PASS Online

Theoretical biological activity range of biocides was forecast in PASS Online. This software evaluates the probability of chemical compound activity based on broad literature data. The obtained bioactivity values of the synthesized biocides are listed in Table 4.

Table 2. *Artemia salina* death rate on XC-720 enamel coatings containing 5, 10 or 20 mass.% biocides — nitroxynil (N), ioxynil (I) and 2,5-dibromo-4-nitrophenol (P), and on the biocide-free coating surface (K) and XC-5226 (M)antifouling copper-containing paint coating

Sample No.	Time from the start of test, h			Average	Performance %
	1	3	5		
N 5.1	17	40	50		
N 5.2	26	60	75	62.5	60.53
N 10.1	85	100	100		
N 10.2	79	97	100	100	100
N 20.1	90	100	100		
N 20.2	75	95	100	100	100
I 5.1	70	95	100		
I 5.2	80	100	100	100	100
I 10.1	75	90	100		
I 10.2	80	100	100	100	100
I 20.1	60	80	95		
I 20.2	65	95	100	97.5	97.37
P 5.1	70	90	100		
P 5.2	65	87	100	100	100
P 10.1	50	70	90		
P 10.2	55	83	95	92.5	92.11
P 20.1	75	95	100		
P 20.2	78	98	100	100	100
K 1	5	10	20		
K 2	10	15	20	20	15.79
M 1	10	20	40		
M 2	0	10	30	35	31.58
Control	0	0	5	5	

Table 3. *Artemia salina* death rate on XC-436 enamel coatings containing 1, 3 or 5 mass.% N, I or P biocides, and on the biocide-free coating surface (K) and XC-5226 (M) antifouling copper-containing paint coating

Sample No.	Time from the start of test, h				Average	Performance, %
	1	3	5	Day		
N 1.1	3	20	65	65		
N 1.2	5	15	60	60	62.5	60.53
N 3.1	5	15	60	95		
N 3.2	10	15	65	80	62.5	60.53
N 5.1	10	60	85	97		
N 5.2	15	60	90	98	87.5	86.84
I 1.1	5	20	25	50		
I 1.2	10	15	20	40	22.5	18.42
I 3.1	20	20	20	85		
I 3.2	20	20	25	90	22.5	18.42
I 5.1	25	40	50	97		
I 5.2	30	40	45	98	47.5	44.74
P 1.1	5	20	40	65		
P 1.2	5	15	35	50	37.5	34.21
P 3.1	5	25	45	60		
P 3.2	10	20	40	60	42.5	39.47
P 5.1	10	30	45	90		
P 5.2	15	30	45	95	45	42.11
K 1	0	0	0	0		
K 2	0	0	0	0	0	0
M 1	0	0	0	0		
M 2	0	0	0	0	0	0
Control	0	0	5	10	7.5	

Table 4 shows that all three biocides theoretically demonstrate wide biological activity range. They can degrade metabolism, energy transfer processes in organism cells, and cell fission process. According to numerical values of compound activity probability (Pa^*), Ioxinil is the most efficient inhibitor. For example, it will inhibit NADPHN-Cytochrome-c2 reductase with probability close to unity, while for N and P, activity probability is lower and equal to 0.781 and 0.663, respectively. Thus, theoretical assessment of biological activity of the synthesized set of biocides has shown that ioxynil is the most active compound (is an inhibitor with probability close to unity). It is also known that ioxynil inhibiting effect may be due to: „...among other things, Hill reaction inhibition and uncoupling of oxidative phosphorylation through photosystem inhibition" [9,10].

It should be noted that the mechanism of biocide effect on hydrobionts requires further investigation both theoretical and practical.

2.4. Assessment of coating strength properties

Average (by 10 measurements) thicknesses of XC-436 enamel composite coatings are listed in Table 5. It is shown that the average coating thickness is virtually unchanged with increase in biocide content in the composition, and it is twice as low as that of the reference sample, which

Table 4. Forecasting biological activity manifestation probability in biocides(maximum probability — unity)

Biocide	Activity	Pa^*	Pi^{**}
Nitroxynil (N)	Vanilloid agonist 1	0.890	0.001
	antianginal	0.800	0.005
	NADPHN-Cytochrome-c2 reductase inhibitor	0.781	0.008
	CYP2C12 substrate	0.784	0.040
	anti-inflammatory agent	0.715	0.014
	Thyroxine 5-deiodinase inhibitor	0.683	0.001
	centromere-associated protein inhibitor	0.661	0.011
	nicotinamidase inhibitor	0.560	0.004
Ioxynil (I)	NADPHN-cytochrome-c2 reductase inhibitor	0.926	0.002
	CYP2C12 substrate	0.913	0.009
	nicotinamidase inhibitor	0.897	0.002
	dextranase inhibitor	0.897	0.003
	centromere-associated protein inhibitor	0.886	0.003
	Thyroxine 5-deiodinase inhibitor	0.823	0
	Acylphosphatase inhibitor	0.751	0.003
	NADPHN peroxidase inhibitor	0.741	0.021
2,5-dibromo-4-nitrophenol (P)	Ferulesterase inhibitor	0.868	0.006
	Phosphatidylserine decarboxylase inhibitor	0.855	0.003
	pectate lyase inhibitor	0.793	0.003
	Antianginal	0.748	0.006
	NADPHN peroxidase inhibitor	0.741	0.021
	CoA fatty-acid synthase inhibitor	0.698	0.012
	Renal function stimulator	0.660	0.019

Note. Pa^* (probability „to be active") — probability that the compound is active; Pi^{**} (probability „to be inactive)" — probability that the compound is inactive.

Table 5. Thickness of composite coatings based on XC-436 enamel containing biocides N, I or P in concentrations 1, 3 or 5 mass.%, XC-5226 (M) antifouling copper-containing paint and biocide-free sample (Reference)

Sample	thickness, mm	Sample	Thickness, mm	Sample	Thickness, mm	Sample	Thickness, mm
N1	0.13	I1	0.13	P1	0.14	M	0.17
N3	0.11	I3	0.17	P3	0.15	Control	0.33
N5	0.11	I5	0.12	P5	0.15		

Table 6. Impact strengths (tests using „Konstanta U-1A") (height, cm) of composite coatings based on XC-436 enamel containing biocides N, I or P in concentrations 1, 3 or 5 mass.%, XC-5226 (M) antifouling copper-containing paint and biocide-free sample (Reference)

Sample	Height, cm	Sample	Height, cm	Sample	Height, cm	Sample	Height, cm
N1	25	I1	12	P1	14	M	7
N3	11	I3	13	P3	15	Reference	50
N5	10	I5	18	P5	15		

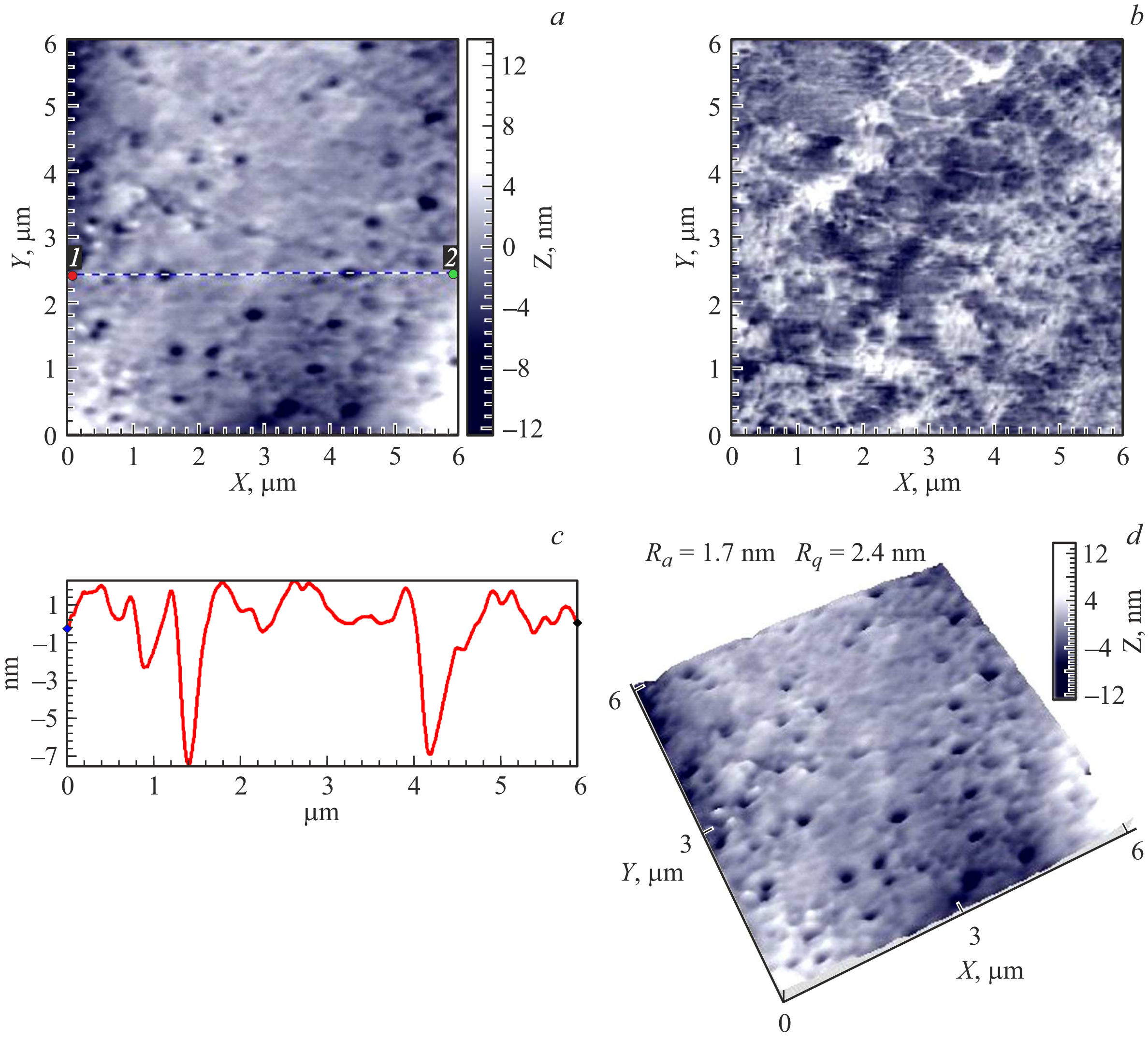

Figure 3. AFM images of polymer base film surface of vinyl chloride-vinyl acetate copolymer (XC-720 enamel) without biocides (reference sample), free surface (top): *a* — topography, *b* — lateral force contrast, *c* — selected surface area profile, *d* — 3D image.

indicates significant decrease of viscosity and improvement of biocide-containing composite coating coverage compared with initial enamels.

Impact strengths of composite coatings based on vinyl and epoxy resin copolymer are listed in Table 6.

Reference sample (biocide-free coating) showed high strength without deformations after load drop from 50 cm. On the other hand, biocide introduction reduces coating strength properties by a factor of 2–3. It has been detected that introduction of 1 mass.% nitroxynil caused coating strength reduction by a factor of two from 50 to 25 cm (Table 6). Further increase in N concentration caused coating strength reduction by another factor of two from 25 to 11–12 cm.

It is interesting to note that introduction of ioxynil reduces coating strength by about factor of 4 from 50 to 12 cm as early as at 1 mass.%, and 2,5-dibromo-4-nitrophenol reduces it from 50 to 14 cm. In this case, P content within 1–5 mass.% in the composition does not influence the coating strength (within measurement error), and content of 5 mass.% nitroxynil even increases the coating strength a little (18 cm). Testing of the coating based on antifouling copper-containing paint (M) has shown low strength of the paint — 7 cm, compared with all tested compositions.

Thus, the biocide-free reference sample has shown high strength. Biocide introduction reduced coating impact strength properties by a factor of 2–3. In this case, increase in nitroxynil content percentage in the coating reduced strength properties, and for ioxynil —increased them a little. For compositions with 2-5-dibromo-4-nitrophenol remained the same within the experiment error. XC-5226 antifouling copper-containing paint has shown low strength values.

Such results suggest that mechanism of interaction between synthesized biocides and polymer matrixes of different nature is very different. Structuring influence of some biocides on supramolecular structure of formed

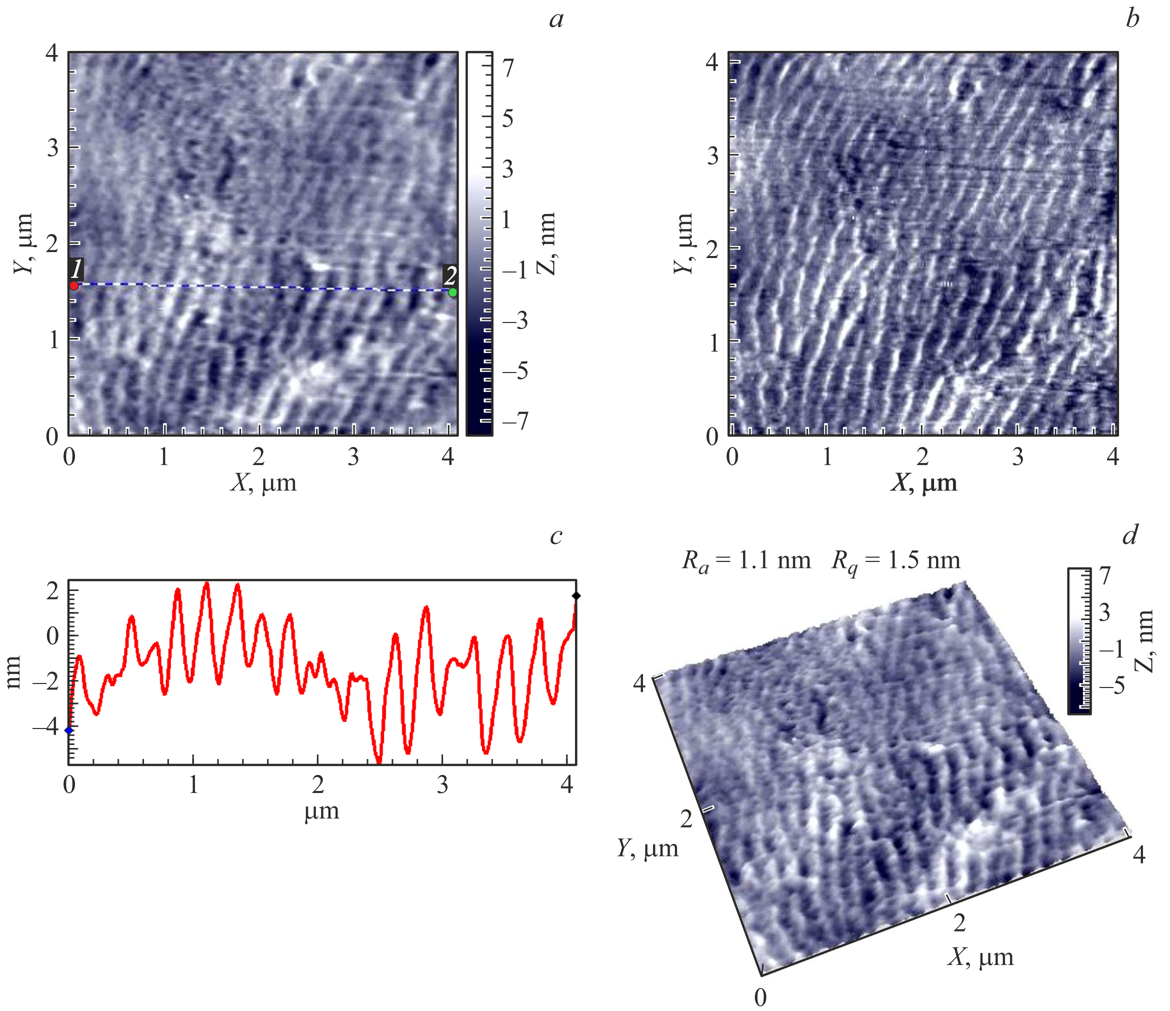

Figure 4. AFM images of vinyl chloride-vinyl acetate copolymer film surface (XC-720 enamel) + 5 mass.% ioxynil (nanostructured composition), free surface (top): *a* — topography, *b* — lateral force contrast, *c* — selected surface area profile, *d* — 3*D* image.

composite coatings is possible because the used biocides are highly crystallized substances which are capable of co-crystallizing with polymer matrix and of forming nano- and microcrystals which can serve as nucleates — nucleating seeds, during film composition drying. To answer this question, composite coating surface investigation carried out using AFM method.

2.5. Determining structural-morphological parameters of coatings

Figure 3 shows AFM images of the initial coating surface fragment based on vinyl chloride-vinyl acetate copolymer (XC-720 enamel). It can be seen that the coating surface has pores evenly distributed throughout the surface. 3*D* image shows that the pore depth is about 10 nm, and diameter is 100–250 nm. Arithmetic mean and root-mean-square surface roughness (R_a and R_q) are 1.7 and 2.4 nm, respectively.

When ioxynil is introduced in XC-720 polymer matrix, surface relief is changed at nanolevel (Figure 4). A regular strip — groove system (so called „wrinkled" surface) has been detected with a width about 200–300 nm and a length of several dozens μm. Height of these strips reaches 5–7 nm. Surface roughness parameters in this case are $R_a = 1.1$ and $R_q = 1.5$ nm. Thus, ioxynil introduction causes nanostructuring and smoothing of coating surface layers. It should be noted that no pores have been found in this coating.

When nitroxynil is introduced in the polymer base, significant sample morphology change is observed. The AFM image of the surface topography (Figure 5) shows granular film texture, grain size is 300–600 nm. It can be assumed that grains are formed by nanocrystals of this biocide coated by polymer matrix, i.e. granular surface morphology is formed. And the surface roughness grows significantly (approximately by an order of magnitude) and is equal to $R_a = 9$ and $R_q = 11$ nm, respectively.

According to the AFM image analysis, it can be concluded that biocide introduction in various polymer matrices has a significant effect on the morphology of the surface to

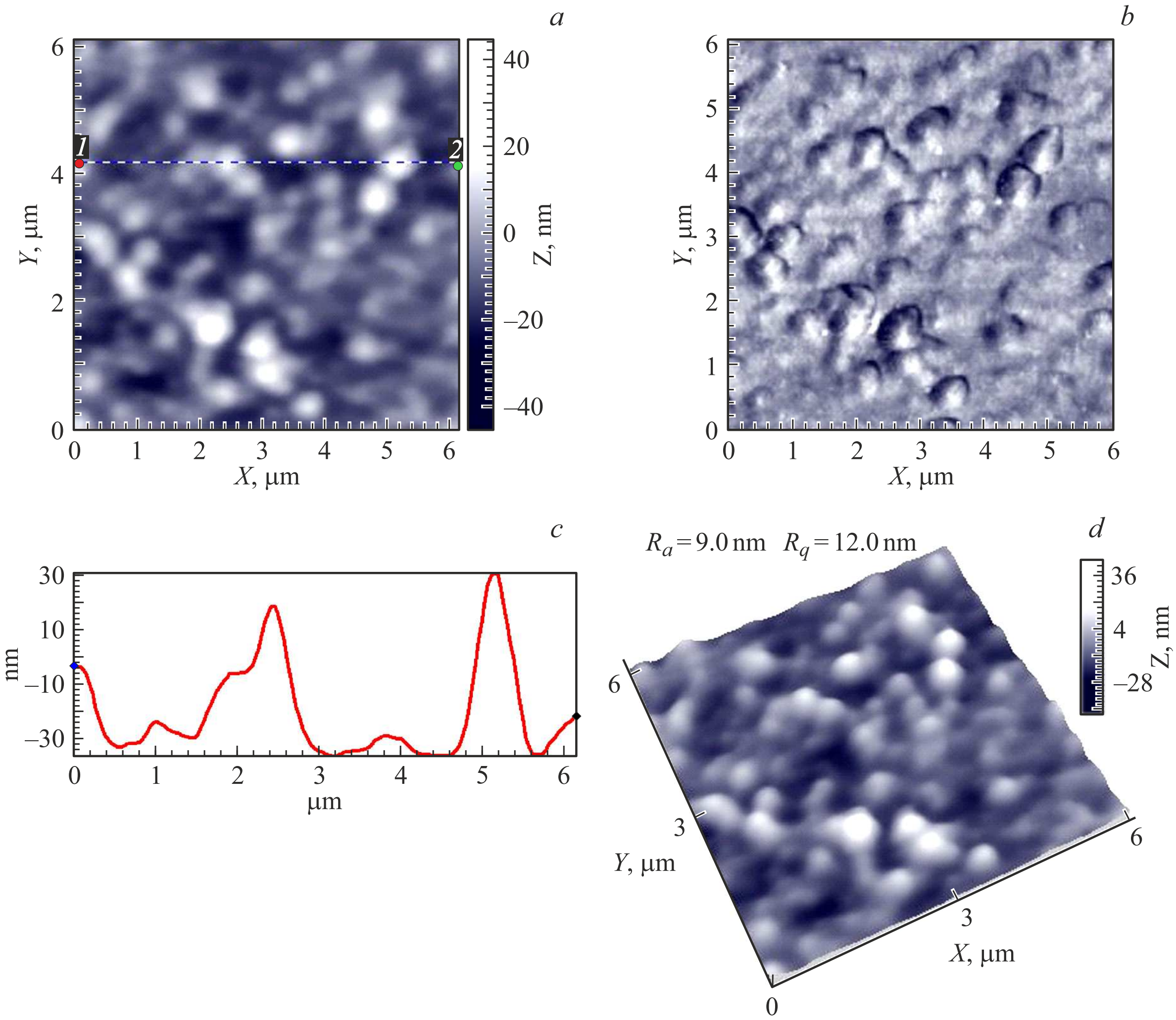

Figure 5. AFM images of vinyl chloride-vinyl acetate copolymer film surface (XC-720 enamel) + 5 mass.% nitroxynil (nanostructured composition), free surface (top): *a* — topography, *b* — lateral force contrast, *c* — selected surface area profile, *d* — 3*D* image.

be formed and causes nanostructuring and change of the surface coating layer relief.

Conclusion

Analysis of a set of iodine- and bromine-containing compounds synthesized in JSC NPO „Iodobrom" (Saki, Crimea) and evaluation of their water solubility have shown that they are poorly soluble, therefore they may be used as biocides introduced in protective and antifouling coating. Composite coatings have been obtained by introduction of three types of biocides: nitroxynil (N), ioxynil (I) and 2,5-dibrommo-4-nitrophenol (P) into anticorrosion PWM of various chemical nature — XC-720 and XC-436 anticorrosion enamels. On the basis of biological activity test using *Artemia salina*, screening analysis of the biological activity of the developed coatings has been carried out by crustaceans survival rate criterium. XC-5226 industrial antifouling copper-containing paint was used as a reference sample.

It has been shown that XC-720 enamel coatings containing Nitoxynil and 2,5-dibromo-4-nitrophenol biocides in concentrations from 5 to 20 mass.% has maximum biological activity (coating performance was equal to 100%), coatings with ioxynil were less efficient: nauplii death achieved 60% at minimum concentration of this biocide in composite coating.

Biocides were introduced in XC-436 enamel in various concentrations from 1 to 5 mass.%. In this case, coatings with N have also shown the highest performance from 60 to 86%. In contrast, performance of coatings with I and P did not exceed 40% in biological tests. Thus, nitroxynil has shown the highest biological activity in all tests on *Artemia salina.*

Comparison of impact strength properties of composite coatings with different biocide content (1 to 5 mass.%) has shown reduction of their strength compared with biocide-free coating. AFM morfology study of the developed coatings and comparison of their strength properties have shown that biocide introduction caused coating structuring at nanolevel, and the strength of biocide-containing coatings is decreased by a factor of 2−3 , however, these values are 2 times higher than the strength values for the reference sample — industrial antifouling copper-containing paint coating.

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Conflict of interest

The authors declare that they have no conflict of interest.

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