

## SEACRAFT HULLS PROTECTION WITH Ti, Cu - BIOCIDAL PIGMENTS

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### Abstract

The main directions of creating new forms of anti-fouling coatings for hulls of sea vessels lie in the field of obtaining an optimal biocide or mixture of biocides. Copper (I) oxide and copper-containing compounds are currently used as the main biocide in such compositions. To obtain competitive biocides containing copper (I) oxide, it is necessary to use relatively cheap inert fillers. The authors proposed a method for producing pigments based on titanium (IV) phosphate and copper compounds that have toxic effect on marine microorganisms for use in coatings that prevent biofouling of ship hulls in seawater. It is shown that by varying the initial ratio of Cu (II) : Ti (III) in the composition of the pigment, the order of mixing, and the temperature of heat treatment of the pigment, it is possible to change the content of various copper compounds in the polymer matrix of titanium phosphate. The obtained samples were studied using the X-ray diffraction, differential scanning calorimetry, scanning electron microscopy methods and other. Thermal transformations of titanium (IV) phosphate samples containing copper in different oxidation states were studied by thermal synchronic analysis in air and nitrogen.

The conditions for obtaining a pigment with a maximum content of copper (I) oxide, necessary for prolonged inhibition of fouling, were found. The ability of the compositions to leach copper and phosphate ions in distilled water and in water similar in composition to seawater, depending on the conditions of heat treatment, was studied. Evaluation tests of the biocidal activity of the obtained pigments in relation to ciliates *Tetrachimena piriformis* and test cultures of bacteria *Staphylococcus aureus*, *Bacillus subtilis* were carried out.

*Key words:* antifouling pigments; biocidal properties; titanium phosphate; copper (I) and (II) compounds.

## Introduction

To protect the hulls of ships from fouling, special anti-fouling materials containing toxic components are used. The effect of anti-fouling coatings is that during operation they gradually dissolve, and their toxic components prevent the attachment of organisms to the hull skin or kill them. Compounds of copper, mercury, zinc, arsenic, tin, lead, and some organic compounds are used as toxins [Railkin, 1998; Gurevich et. al., 1989; Sheshukov et. al., 1992; Kopylov, 2011]. The solubility of toxins should provide concentration in the layer of water in contact with the treated surface of the hull to be sufficient to protect the hull from fouling.

The mechanism of the protective action of anti-fouling coatings is based on the leaching of the biocide (pigment). Leaching is the process of dissolving (washing out) soluble components from a protective coating. The effectiveness of the anti-fouling composition is proportional to the biocide content of the coating. For each biocide, there is a critical leaching level where the biocide remaining in the film no longer provides antifouling protection. The rate of leaching of the biocide is also affected by the thickness of the coating layer [Zobachev, 1984]. Traditionally, anti-fouling materials are produced mainly on vinyl and chlorinated rubber bases, as well as rosin. Compounds containing lead, mercury, arsenic and tin were previously used as biocides in them, which are currently prohibited for use. Examples of such coatings are presented in patents [Gurevich, 1983; Karpov, 2010; ZAO «HIMEKO-GANG», 1998; Braeken et. al., 1990; Matsuo, 1990; Camp, 2004]. The main directions of creating new forms of antifouling coatings lie in the field of obtaining an optimal biocide or a mixture of biocides and creating a carrier with a controlled release of biocides for five or more years. Only the most potent biocides are suitable for this purpose. Copper (I) oxide and other copper-containing compounds are currently used as the main biocide in such compositions [Baxter, 1987]. Copper (I) oxide has a solubility value of  $5.4 \mu\text{g}/\text{cm}^3$  in seawater at pH 8.1, which ensures a long-term transfer of this biocide into seawater with a concentration that is lethal to marine organisms. This solubility of copper (I) oxide in seawater is achieved after an induction period, which, depending on the ambient temperature and pH of seawater, can last up to 3 months.

One of the main organic polymers used to obtain antifouling coatings with copper (I) oxide is rosin [Baxter, 1987; Beznosov et. al. 2013]. The mechanism of action of such a coating is based on the solid-phase reaction of copper oxide with rosin to form copper resinates, readily soluble in seawater, which then interact with chlorides dissolved in seawater, forming toxic compounds. In addition to rosin, the coating may include organic hydroxy acids, organic acid anilides, mineral pigments, plasticizers and organic solvents. Salicylic, tartaric, malic acids are used as organic hydroxy acids in the proposed compositions, and dibutyl phthalate, tricresyl phosphate,

polyisobutylene are used as plasticizers; zinc oxide, iron minium are used as mineral pigments; copper monoxide, cupric rhodanide are used as copper-containing biocides; organic solvents - solvent, xylene, petroleum spirit. Also known are compositions that include, in addition to the above components, polymeric film-formers - a copolymer of vinyl chloride with vinyl acetate, epoxy resin and epoxy ester varnish, as organic solvents - acetone, cyclohexanone, etc. [Karpov, 2010; Beznosov, 2013].

To obtain competitive pigments containing Cu (I), it is necessary to use relatively cheap inert fillers. As such a filler, we have chosen previously not used for these purposes X-ray amorphous titanium phosphate  $Ti(HPO_4)_2 \cdot nH_2O$ , the synthesis of which in a solution of phosphoric acid, sorption properties and chemical stability are well known [Maslova, 2006; Shablovski, 1983]. This particular filler was chosen for several reasons. Firstly, this material is known to be a good anticorrosive pigment, which is widely used in world practice. Secondly, as it is known, the world accumulates sufficiently large amounts of titanium metal waste, which cannot be recycled by traditional metallurgical methods, but is easily converted into salts of this metal. In this regard, it is promising to use waste metal titanium as a cheap source of trivalent and tetravalent titanium compounds for the production of cheap pigments based on titanium phosphate.

The aim of this work is to develop a method for producing a pigment based on titanium phosphate with high content of copper oxide and to prove the possibility of its use in antifouling compositions.

## Materials and Methods

Trivalent titanium phosphate was obtained by dissolving titanium metal in 20% orthophosphoric acid at 105 °C for 4 h in the presence of a catalyst according to our method [Shablovski, 1983].

In this work, the interaction of  $CuCl_2 \cdot 2H_2O$  with  $TiPO_4$  was studied in various molar ratios. It was assumed that Ti (III) would exhibit reducing properties and the pigment would thus include cuprous compounds in a tetravalent titanium phosphate matrix. To obtain a pigment of the required composition, the Cu (II) : Ti (III) ratio, the order of mixing the components, and the drying modes of the obtained samples were varied during the synthesis. Samples were prepared by mixing under normal conditions 1 M solutions of  $CuCl_2$  and  $TiPO_4$  at a molar ratio of copper to titanium from 1 : 2 to 1 : 5. The resulting solutions were stirred with a magnetic stirrer for 25 min. The precipitate was separated from the solution by decantation, filtered on a Buchner funnel, and dried at 70 – 80 °C. The resulting pigment samples were heated in air at temperatures of 160, 215, and 260 °C.

X-ray diffraction studies of the obtained samples were performed using a DRON-3.0 diffractometer ( $CoK_\alpha$  -radiation, Mn-filter). The recording speed in the angular range  $2\theta = 3-60^\circ$  was 1 deg/min. To decode the X-ray diffraction patterns and obtain the quantitative characteristics of the obtained compounds, the data were entered into a special computer program MATH, based on the PDF-2 X-

ray diffraction databases of the ICCD company. The content of the components (%) was determined using reference intensity ratio of the maximum peaks characteristic for the isolated phases.

Thermal analysis of the samples was carried out by differential scanning calorimetry on an STA 449 C Jupiter synchronic thermal analyzer (NETZSCH, Germany) in air and in nitrogen atmosphere.

The morphology of pigment powders was studied by scanning electron microscopy (SEM, microscope LEO-1420). X-ray energy dispersive microanalysis was performed on the same instrument with a Roentec attachment.

Leaching of copper ions and phosphate ions was carried out in distilled water and in a solution imitating seawater of the composition (g/dm<sup>3</sup>): NaCl - 10.0; MgSO<sub>4</sub> - 1.0 according to the following method. Pigment samples weighing 100.0 mg were placed in 10.0 cm<sup>3</sup> of distilled water or a solution of simulated seawater, kept for 7 days, after which the content of copper ions and orthophosphate ions in the settled solutions was analyzed. The pH of the resulting solutions was determined using an I-160MP laboratory ionomer. The arithmetic mean of the results of three parallel determinations, the difference between which did not exceed 0.1 pH units, was taken as the test result.

The determination of copper was carried out on an atomic emission spectrometer with inductively coupled plasma "ACTIVIA M" (France).

The phosphorus content was determined by the colorimetric method by the yellow color of the phosphorus vanadate-molybdate complex on a KFK-3-01 photoelectric photometer at  $\lambda = 460$  nm.

The toxicity of the test samples was determined according to the "Methodological Guidelines for the Toxic-Biological Evaluation of Meat, Meat Products and Milk Using *Tetrachimena Piriformis* Ciliates" by the presence of dead and surviving ciliates, changes in the shape and growth inhibition of *Tetrachimena piriformis* at the S. N. Vysheskiy Institute of Experimental Veterinary Medicine of NAS Belarus according to the following method. A certain amount of pigments was added to tubes containing a nutrient medium and a certain number of ciliates, shaken thoroughly, and left at room temperature for 24 hours in a dark place. During the day, the test tubes were shaken 3-4 times in order to aerate the medium and stir up the settled particles of the test material. After 1, 6, 24, and 96 hours, inoculation samples from each tube were examined under an optical microscope. The presence of dead or deformed cells, deceleration and change in the nature of movement, inhibition of the growth and reproduction of ciliates in comparison with the control indicated the toxicity of the test material. Evaluation of toxicity in relation to ciliates *Tetrachimena piriformis* was carried out on a 4-point system. A decrease in the degree of reproduction of protozoa by 20–30% indicated the presence of weak toxicity (1 point). The suppression of reproduction of ciliates up to 30% with a simultaneous decrease in movement activity, violation of its character and the presence of up to 10% of altered cells indicated a moderate degree of toxicity (2 points). Decrease in the degree of reproduction of ciliates by 30–50% with the simultaneous presence of 10–20% of cells with

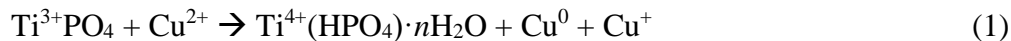
disturbances in the nature of movement, shape and dead ciliates indicated the expressed toxicity of the product (3 points). And, finally, a decrease in the degree of reproduction of ciliates by 50% and more, the presence of cysts, deformed cells (in particular in the form of drumsticks, etc.) indicates a strong toxicity of the product (4 points).

In the same place, the biocidal (antimicrobial) activity was rated by the method of serial dilutions in relation to test cultures of bacteria *Staphylococcus aureus*, *Bacillus subtilis*. The resistance of test microbes of bacteria *Staphylococcus aureus*, *Bacillus subtilis* to the obtained samples was studied by diffusion into agar using wells in the thickness of the agar (bacteriostatic activity). The presence of a zone of inhibition of microbial growth around the wells and its size were indicators of the sensitivity of the test culture to the test samples.

## Results and discussion

Table 1 shows the phase composition of copper compounds in the composition of pigments obtained at different molar ratios of Cu (II) : Ti (III) in the initial solutions and temperatures of heat treatment. As can be seen from the table, the transformation products of copper compounds are Cu, Cu<sub>2</sub>O, CuO, CuCl, Cu<sub>2</sub>(OH)<sub>3</sub>Cl, Cu<sub>2</sub>Cl(OH)<sub>3</sub>, etc.

Studies have shown that, because of redox reactions in the CuCl<sub>2</sub>·2H<sub>2</sub>O : TiPO<sub>4</sub> system, Cu (II) is reduced to Cu (I) and Cu (0). A diagram of the ongoing processes can be represented in the form of equations:



In the case of the Cu (II) : Ti (III) ratio 1 : 2, copper (I) compounds are not formed in the entire tested temperature range. As the ratio increases from 1 : 3 to 1 : 4.5, the amount of Cu<sub>2</sub>O increases. The highest content of Cu<sub>2</sub>O (56.4%) was noted at the Cu (II) : Ti (III) ratio 1 : 4.5 (sample #5). When studying the dependence of the amount of Cu<sub>2</sub>O on the processing temperature, it was found that with an increase in the specified ratio from 1 : 3.5 to 1 : 4.5, the content of Cu<sub>2</sub>O in the samples increases to 99.6%.

It was determined [Shablovski, 1983] that titanium in the pigments obtained is in the form of titanium (IV) hydrophosphate Ti(HPO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O crystalline hydrate, which is formed as a result of oxidation of Ti (III) phosphate to Ti (IV). According to the literature [Sarawadekar, 1983], crystalline hydrate Ti(HPO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O is X-ray amorphous up to 600 °C and loses water of crystallization at 160 °C, which is confirmed by the results of the X-ray phase analysis. We did not observe the diffraction peaks of titanium compounds in the X-ray diffraction patterns of samples 1-6 obtained by us both before and after heating. As an example, Fig. 1 shows a line X-ray diffraction pattern of sample #5, obtained at room temperature, from which it follows that only crystalline phases of copper compounds are present in the pigment samples.

All the samples obtained were studied by the method of synchronic thermal analysis when heated to 800 °C.

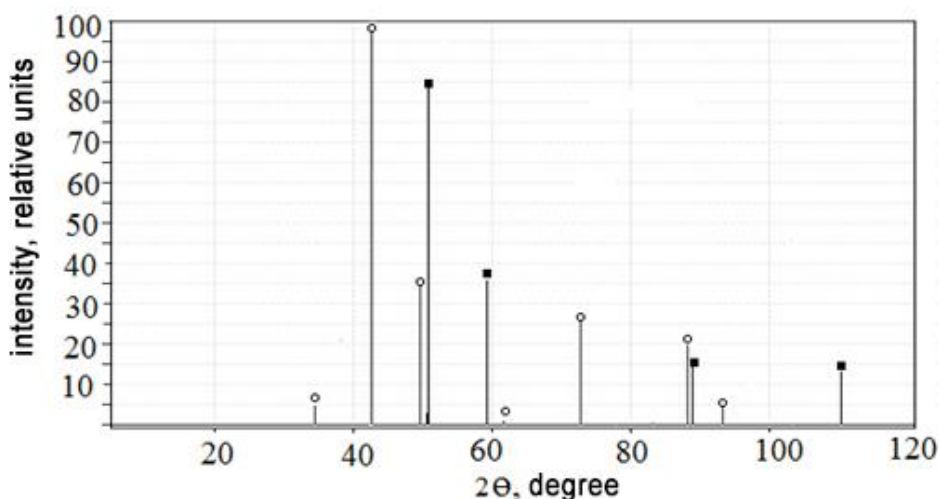
**Table 1.** Phase composition of copper compounds depending on the Cu (II) : Ti (III) ratio and air heat treatment temperatures

Sample (Cu(II) : Ti(III) ratio)	Temperature, °C	Phase composition	Content of components, %
1	2	3	4
№ 1 (1 : 2)	20	Cu <sub>2</sub> (OH) <sub>3</sub> Cl	54.1
		Cu <sub>2</sub> Cl(OH) <sub>3</sub>	45.9
	160	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	49.3
		Cu <sub>2</sub> (OH) <sub>3</sub> Cl	30.3
		(CuCl <sub>2</sub> )(Cu(OH) <sub>2</sub> ) <sub>3</sub>	20.4
	260	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	90.4
CuO		9.6	
№ 2 (1 : 3)	20	Cu <sub>2</sub> O	13.3
		CuCl	61.8
		Cu	24.9
	160	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	33.6
		Cu <sub>2</sub> O	32.2
		CuCl	14.3
		Cu	19.9
215	Cu(OH) <sub>2</sub>	19.7	
	CuO	32.4	
	CuCl <sub>2</sub> (Cu(OH) <sub>2</sub> ) <sub>3</sub>	30.5	
	CuCl	17.4	
	260	Cu <sub>2</sub> Cl(OH) <sub>3</sub>	51.9
CuO		48.1	
№ 3 (1 : 3.5)	20	Cu <sub>2</sub> O	3.8
		Cu	96.2
	160	Cu <sub>2</sub> O	7.3
		Cu	92.7
	215	Cu <sub>2</sub> O	25.5
		Cu	74.5
	260	Cu <sub>2</sub> O	70.9
		CuO	21.6
		Cu	7.5
№ 4 (1 : 4)	20	Cu <sub>2</sub> O	4.5
		Cu	95.5
	160	Cu <sub>2</sub> O	5.7
		Cu	94.3
	215	Cu <sub>2</sub> O	21.1
		Cu	78.9
	260	Cu <sub>2</sub> O	58.2
		CuO	30.7
Cu		11.0	

**Table 1.** Phase composition of copper compounds depending on the Cu (II) : Ti (III) ratio and air heat treatment temperatures (*continuation*)

№ 5 (1 : 4.5)	20	Cu <sub>2</sub> O	56.4
		Cu	43.6
	160	Cu <sub>2</sub> O	60.5
		Cu	39.5
	215	Cu <sub>2</sub> O	81.4
		Cu	18.6
260	Cu <sub>2</sub> O	99.6	
	CuO	0.4	
№ 6 (1 : 5)	20	Cu <sub>2</sub> O	52.3
		Cu	47.7
	160	Cu <sub>2</sub> O	60.3
		Cu	39.7
	215	Cu <sub>2</sub> O	78.8
		Cu	21.2
	260	CuO	44.1
		Cu <sub>2</sub> O	28.9
		Cu	27.0

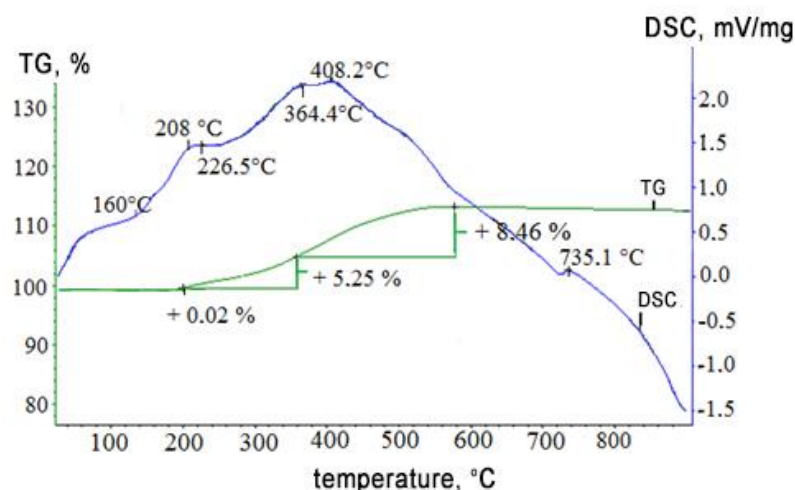
Fig. 2 presents the data of thermal analysis of the dried, but unheated pigment (#5), obtained at the Cu (II) : Ti (III) ratio 1 : 4.5, which, according to the data in table 1, ensures the formation of Cu (I) compounds in the maximum amount in air atmosphere.



**Fig. 1.** Line X-ray diffraction pattern of sample #5: ○ – Cu<sub>2</sub>O, ■ – Cu<sup>0</sup>.

The TG curve indicates no change in mass in the temperature range of ~ 80–160 °C, a small increase in mass in the range 160–360 °C, and a slightly more intense increase at 360–560 °C.





**Fig. 2.** TG and DSC curves of sample #5 in air atmosphere.

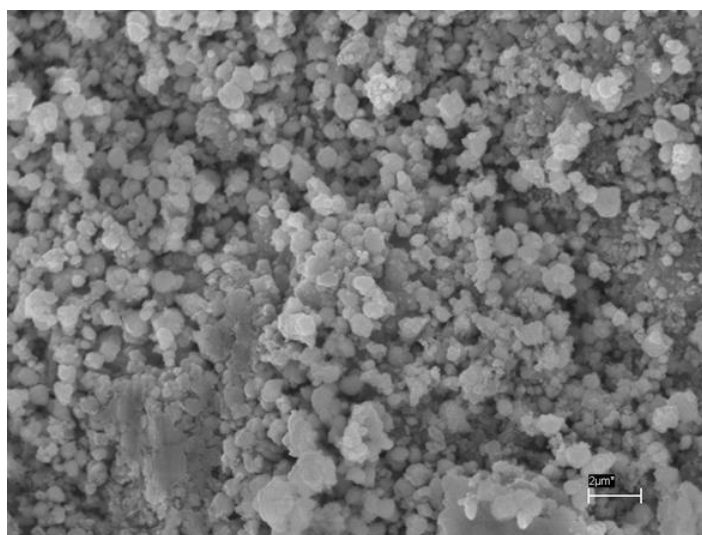
It may be due to the oxidation of Cu and Cu<sub>2</sub>O to CuO. The peaks observed on the DSC curve may indicate a stepwise oxidation process. The shape of the DSC curve helped to justify the choice of heating temperatures for the samples (see Table 1). So, the 160-215 °C interval corresponds to intensive oxidation of copper in the pigment sample, and 260 °C corresponds to the beginning of the second peak of intense oxidation.

On the DSC curve in a nitrogen atmosphere, no obvious exo- and endo-effects were observed, and on the TG curve, a small (~ 3.0%) weight loss of the sample is observed, which corresponds to the removal of crystallization water from titanium phosphate. No oxidation of copper compounds occurs.

Based on the results of the experiments, a pigment sample heated at a temperature of 260 °C with a maximum content of copper (I) oxide Cu<sub>2</sub>O (99.6%) was selected for further studies (sample #5).

The most important characteristics of pigments are their uniformity and degree of dispersion. Therefore, the morphology of the obtained powders was evaluated. According to the SEM data of sample #5 (see Table 1) heated at 260 °C, its surface is uniform, with particle sizes around 0.5 – 1 μm (Fig. 3). This dispersion of the pigments is an important characteristic, indicating that the material does not require further grinding.





**Fig. 3.** SEM-image of the sample #5, heated at 260 °C with 99,6 % copper (I) oxide content.

For further study of the properties of pigments, experiments were carried out on the leaching of copper ions and phosphate ions from pigment samples obtained at room temperature (sample #5A) and with heat treatment at temperatures: 160 °C (sample #5B), 215 °C (sample #5C), and 260 °C (sample #5D), in distilled water and water similar in composition to sea water.

The pH values of the obtained solutions were determined during the leaching process. From table 2 it follows that the concentration of copper ions after leaching in water similar in composition to sea water is significantly higher than in distilled water, and for pigment samples heated at 160 - 260 °C, 155.6 - 209.9 mg/dm<sup>3</sup> respectively. It should be noted that the leachability of copper ions is quite high. The concentration of phosphate ions in leaching solutions for an unheated sample and samples obtained during heating decreases with an increase in the processing temperature from 33.0 to 0.0 mg/dm<sup>3</sup>. The obtained leaching solutions are weakly acidic with similar pH values in the range of 4.3-4.8.

**Table 2.** Concentration of copper and phosphate ions after leaching for 7 days

Sample #, solvent	Temperature of treatment, °C	Initial pigment composition	Content of component in pigment, %	Cu(II) ions concentration in solution, mg/dm <sup>3</sup>	PO <sub>4</sub> <sup>3-</sup> ions concentration, mg/dm <sup>3</sup>	pH
#5A, dist. water	20	Cu <sub>2</sub> O Cu	56.4 43.6	89.1	28.0	4.5
#5B, dist. water	160	Cu <sub>2</sub> O Cu	60.5 39.5	94.8	24.0	4.7
#5C, dist. water	215	Cu <sub>2</sub> O Cu	81.4 18.6	111.3	19.5	4.7
#5D, dist. water	260	Cu <sub>2</sub> O CuO	99.6 0.4	118.0	0.1	4.8
#5A, salt. water	20	Cu <sub>2</sub> O Cu	56.4 43.6	155.6	33.0	4.4

**Table 2.** Concentration of copper and phosphate ions after leaching for 7 days (*continuation*)

#5B, salt. water	160	Cu <sub>2</sub> O Cu	60.5 39.5	184.0	28.5	4.7
#5C, salt. water	215	Cu <sub>2</sub> O Cu	81.4 18.6	205.6	23.5	4.5
#5D, salt. water	260	Cu <sub>2</sub> O CuO	99.6 0.4	210.0	0.0	4.3

Evaluation tests of the biocidal activity of the obtained pigments in relation to ciliates *Tetrachimena piriformis* and test cultures of bacteria *Staphylococcus aureus*, *Bacillus subtilis* were carried out.

Table 3 shows the number of multiplied protozoa *Tetrachimena piriformis* in the sample when pigments #5A, 5B, 5C, 5D are added to the culture medium. Samples containing a medium with infusoria without adding a weighed portion of pigment served as control for the analysis.

**Table 3.** Toxicity of pigment samples to *Tetrachimena piriformis* ciliates

Sample	Number of ciliates			
	1 h	6 h	24 h	96 h
Sample #5A	–	–	–	40
Sample #5B	–	–	–	60
Sample #5C	–	–	1	80
Sample #5D	–	–	6	120
Control sample	15	40	60	140

As it can be seen from the table 3, there was no growth of ciliates during the day in the medium with samples 5A and 5B, in the medium with sample 5C one ciliate was observed in the field of view, with sample 5D - 6 ciliates. When ciliates were cultivated at a temperature of 25 ° C for 96 h, the growth of ciliates was observed in all samples. However, in samples 5A and 5B the degree of reproduction of ciliates is less than in the control sample by 71.4% and 57.1%, respectively, which indicates a strong toxicity (4 points). In the sample 5C, the decrease in the degree of reproduction of ciliates in relation to the control sample was 42.9%, which corresponds to pronounced toxicity (3 points). A decrease in the degree of reproduction of ciliates in the sample 5D in relation to the control sample by 14.3% indicates weak toxicity (1 point).

When studying the resistance of the test microbes *Staphylococcus aureus*, *Bacillus subtilis* to the obtained samples of pigments by diffusion into agar using wells in the thickness of the agar, it was found that all samples formed a zone of inhibition of microbial growth (lysis) both on the culture of *Bacillus subtilis* and on the culture of *Staphylococcus aureus* (excl. sample 5A), above 15 mm, which indicates a good bacteriostatic activity of the samples to these test cultures (Table 4).

**Table 4.** Results of studying the bacteriostatic properties of pigment samples in relation to test cultures of bacteria *Staphylococcus aureus*, *Bacillus subtilis*

Sample	Size of lysed zone for bacteria, mm	
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
Sample # 5A	13	23
Sample # 5B	20	16
Sample # 5C	18	22
Sample # 5D	19	17
Medium control	No growth	

## Conclusions

A method is proposed for obtaining pigments with a toxic effect on marine microorganisms, based on titanium (IV) phosphate and copper oxide using redox transformations in solutions containing  $\text{CuCl}_2$  and trivalent titanium phosphate, for use in coatings that prevent biofouling of ship hulls in sea water.

It is shown that by varying the initial molar ratio of Cu (II) : Ti (III) in the composition of the pigment, the order of mixing the solutions, and the temperature of heat treatment of the pigment, it is possible to change the ratio of various copper compounds in the polymer matrix of titanium phosphate. It was found that with an increase in this ratio in the samples obtained, the mass fraction of copper (I) oxide increases and the fraction of elemental copper decreases.

The conditions for obtaining a pigment with a maximum content of copper (I) oxide, necessary for prolonged inhibition of fouling, were found. Such a pigment is obtained with an initial ratio of Cu (II) : Ti (III) components equal to 4.5 and a heat treatment temperature of 260 °C. The  $\text{Cu}_2\text{O}$  content in it is 99.6%, the particles have sizes around 0.5 - 1  $\mu\text{m}$ . The material does not require further grinding.

The ability of the compositions to leach copper ions and phosphate ions in distilled water and in water similar in composition to seawater, depending on the conditions of heat treatment, was studied. It has been shown that the concentration of copper ions in water similar in composition to seawater is significantly higher than in distilled water and is 155.6 - 209.9  $\text{mg}/\text{dm}^3$  for pigment samples heated at 160 - 260 °C, respectively.

Evaluation tests of the biocidal activity of the obtained pigments in relation to ciliates *Tetrachimena piriformis* and test cultures of bacteria *Staphylococcus aureus*, *Bacillus subtilis* were carried out. It is shown that the samples obtained by the proposed method have high biocidal activity.

## Conflict of interests

The authors declare that they have no conflict of interest.

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## ЗАХИСТ КОРПУСІВ СУДЕН Ti, Cu - БІОЦИДНИМИ ПІГМЕНТАМИ

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### Реферат

Основні напрямки створення нових форм протиобростаючих покриттів корпусів морських суден лежать в області отримання оптимального біоциду або суміші біоцидів. В якості основного біоциду в таких композиціях в даний час використовують оксид міді (I) і мідьвмісні сполуки. Для отримання конкурентоспроможних біоцидів, що містять оксид міді (I), необхідно використовувати відносно дешеві інертні наповнювачі. Авторами запропонований метод отримання пігментів на основі фосфату титану (IV) із сполуками міді, що володіють токсичною дією по відношенню до морських мікроорганізмів, для використання в складі покриттів, що перешкоджають біобростанню корпусів суден в морській воді. Показано, що, варіюючи вихідне співвідношення Cu (II) : Ti (III) в складі пігменту, порядок змішування розчинів і температуру термообробки пігменту, можна змінювати зміст різних сполук міді в полімерній матриці фосфату титану. Отримані зразки були вивчені за допомогою рентгенографічного методу, методу диференціальної скануючої калориметрії, СЕМ та інших. Методом термічного синхронного аналізу в повітряній атмосфері і атмосфері азоту вивчені термічні перетворення зразків фосфату титану (IV), що містять мідь в різному ступені окислення.

Знайдено умови отримання пігменту з максимальним вмістом оксиду міді (I), необхідні для пролонгованого гальмування обростання. Вивчено здатність композицій до вилуговування іонів міді і фосфат-іонів в дистильованій воді і в воді, близької за складом до морської залежно від умов термообробки. Проведено оціночні випробування біоцидною активності отриманих пігментів по відношенню до інфузорій *Tetrachimena piriformis* і тест-культур бактерій *Staphylococcus aureus*, *Bacillus subtilis*.

*Ключові слова:* протиобростаючі пігменти; біоцидні властивості; фосфат титану; сполуки міді (I) і (II).