EP-

TECHNOLOGY ORGANIC AND INORGANIC SUBSTANCES

Синтезовано наносрібло методом інтеркаляції іонного срібла в міжшарові порожнини монтморилоніту. Визначено стійкість інтумесцентних покриттів складу поліфосфат амонію/ пентаеритрит/меламін/співполімер етиленвінілацетату/оксид титану з домішками Agформи монтморилоніту по відношенню до цвілевих і деревофарбувальних грибів. Встановлено, що суміш Ag-монтморилоніту з монтморилонітом, модифікованим полігексаметилен гуанідиновим катіоном, забезпечує клас біоцидної ефективності покриття «високоефективний»

Ключові слова: наносрібло, полігексаметиленгуанідин, вогнезахист, монтморилоніт, антибактеріальні покриття, інтумесцентні композиції

Синтезировано наносеребро методом интеркаляции ионного серебра в межслоевые пространства монтмориллонита. Определена устойчивость интумесцентных покрытий состава полифосфат аммония/пентаэритрит/меламин/ сополимер этиленвинилацетата/оксид титана с добавками Ag-монтмориллонита по отношению к плесневым и деревоокрашивающим грибам. Установлено, что смесь Ag-монтмориллонита и монтмориллонита, модифицированного полигексаметиленгуанидиновым катионом, обеспечивает класс биоцидной эффективности покрытия «высокоэффективный»

Ключевые слова: наносеребро, полігексаметиленгуанідин, огнезащита, монтмориллонит, антибактериальные покрытия, интумесцентные композиции

1. Introduction

In the course of development of technological processes and equipment, designing, construction, reconstruction and operation of pharmaceutical enterprises, it is necessary to follow the GMP requirements and safety standards. One of the main criteria for manufacturing medicines is the cleanliness of industrial premises. This predetermines special requirements for walls and internal building structures and, accordingly, to finishing – varnish and paint materials (VPM). In accordance with the provisions of Regulation (EU) No. 305/2011 [1], VPM must meet basic environmental and health standards, as well as fire safety requirements:

 absence of the negative impact of hazardous chemical compounds and components of a coating on human health and environment;

 chemical and environmental safety in the case of fire – restriction of fire and smoke propagation, minimal toxicological impact of combustion products on human health and environment;

UDC 661.174 + 667.6

DOI: 10.15587/1729-4061.2017.107281

EXAMINING THE EFFECT OF NANOSILVER ON THE ANTIBACTERIAL FIRE-RETARDANT COATINGS FOR PHARMACEUTICAL ENTERPRISES

L. Vakhitova PhD, Senior Researcher* E-mail: L.M.Vakhitova@nas.gov.ua

> V. Bessarabov PhD, Associate Professor** E-mail: drvib500@gmail.com

K. Kalafat* E-mail: K.V.Kalafat@nas.gov.ua V. Drizhd Postgraduate Student*

E-mail: drizhd@nas.gov.ua **G. Zagoriy**

Doctor of Pharmaceutical Sciences, Professor** E-mail: Ph.G.Zag@gmail.com *L. M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry National Academy of Sciences of Ukraine Kharkivske shosse str., 50, Kyiv, Ukraine, 02160 **Department of Industrial Pharmacy Kyiv National University of Technologies and Design Nemyrovych-Danchenko str., 2, Kyiv, Ukraine, 01011

- biological safety – prevention of the formation and proliferation of pathogens on the surface, as well as the minimization of biological effects on the human body.

That is why coatings for special purposes, such as antibacterial, fire-retardant and fire-protective, are becoming increasingly popular in the world market of VPM. These coatings have to be applied to meet a whole set of requirements to modern construction and various types of safety.

The most economical and effective approach to the development of new coatings for the enterprises of pharmaceutical industry is the combination of several useful properties in one material. That is why research with a focus on the creation of coatings with a set of antibacterial and fire-retardant qualities is relevant.

2. Literature review and problem statement

Anti-bacterial (anti-microbial) coatings are relatively new functional materials that have bacteriostatic and bactericidal properties. According to the estimates of experts from Transparency Market Research, the world market for antibacterial materials doubles every 5 years. In 2018, it should exceed the level of USD 3 billion [2].

The mechanism of the action of antibacterial agents includes the following aspects:

- interference into the synthesis of a cell wall;

- damage of a cell membrane;
- inhibition of protein synthesis;
- preventing the synthesis of nucleic acids [3].

Antibacterial coatings contain biocidic additives, which are divided into two main types: organic and inorganic. The most common preparations of the organic type, used in antibacterial coatings, are the salts of quaternary ammonium and their derivatives [4, 5]. Biocidic action of this group of substances is aimed at damaging a cell membrane and protein denaturation. Inorganic antibacterial agents usually contain metal ions (silver, zinc, copper) on a non-organic carrier, such as zeolite or clay. The most common biocide admixture to an antibacterial paint is the so-called "nanosilver" [6, 7]. It was proved [8] that nanodimensional biocides act by the mechanisms that can alter completely compared with conventional counterparts that have identical chemical composition. Nanoparticles prolong antibacterial properties of a coating for quite a long time. Antibacterial coatings containing admixtures of nanometals are very effective against bacterial adhesion and growth of bacteria on protected surfaces [6-8]. In many cases, exact mechanisms of the toxicity of nanocompounds for bacteria are not explored sufficiently enough. But there is information on that the nanobiocides are able to get attached to the cell wall of bacteria through electrostatic interactions leading to the destruction of cell membranes [6] and cause oxidative stress due to the formation of free radicals [9].

The majority of antimicrobial paints available in the world market are known to contain nanosilver, which effectively kills different kinds of bacteria: *E. Coli, L. monocytogenes*, salmonella (*S. Typhimurium*), *Staphylococcus aureus*, enterococcus (*E. Faecalis*), blue pus bacillus (*P. aeruginosa*) and others [2]. An example of the results of tests of antimicrobial activity of the paint with nanoparticles of silver is shown in Table 1.

Table 1

Dynamics of bactericidal effect of antimicrobial paint with nanosilver on the strains of bacteria [2]

Strain	Samples*	A**			
Time, hours		0	0.5	1.0	2.0
E. coli	+	$6.0 {\pm} 0.1$	$6.0 {\pm} 0.1$	6.0±0.1	6.0 ± 0.2
E. COll	-	4.2 ± 0.2	0	0	0
S. typhimurium	+	6.1±0.1	6.1±0.1	6.1±0.1	6.0±0.2
5. typnimurium	-	4.3 ± 0.1	0	0	0
S. Aureus	+	$6.0 {\pm} 0.1$	6.0±0.1	6.0±0.1	6.0 ± 0.2
S. Aureus	-	5.3 ± 0.1	0	0	0
E facealia	+	6.1±0.1	6.1±0.2	6.0±0.1	6.0±0.1
E. faecalis	-	$4.3 {\pm} 0.2$	0	0	0
T	+	6.1±0.1	6.0±0.1	6.0±0.1	6.0±0.2
L. monocytogenes	-	$4.4 {\pm} 0.1$	0	0	0
D	+	6.0 ± 0.2	6.1±0.2	6.0±0.1	6.0±0.2
P. aeruginosa	-	5.6 ± 0.2	3.0±0.2	1.0±0.1	0

Note: * - (+) is the reference culture; (-) is the paint with nanosilver; ** - A is the logarithm of the number of living bacteria on the surface of the painted samples over different intervals of time (hours) after the application of bacteria

It should be noted that the scientific literature virtually lacks any information on the coatings for universal purposes, which would provide anti-microbial and fire-retardant properties at the same time. Therefore, the idea of creation of an innovative coating with proven antibacterial action and fire-retardant efficiency is promising and necessary for most objects of modern construction, especially for the premises in pharmaceutical industry. The combination of intumescent fire-retardant and antibacterial technologies with the use of derivatives of montmorillonite (MMT) should solve the task of creation of an effective fire-retardant coating with a high degree of bioresistance [10–13].

3. The aim and objectives of the study

The goal of present research is to study the influence of montmorillonite, modified with ions of silver and quaternary ammonium cations, on the resistance to biodamage of the intumescent composition (IC) of ammonium polyphosphate (APP)/pentaerythrite (PE)/melamine (MA)/copolymer of ethylenevinyl-acetate (EVA).

To achieve the set goal, the following tasks had to be fulfilled:

 to determine biocidic activity of montmorillonite with cations of silver as part of intumescent coating;

- to test fire-protection efficiency of the intumescent coatings containing modified nanoclays.

4. Materials and methods of examining the influence of organoclays on the formation and physical characteristics of coke layer

4.1. Materials and equipment used in the experiment

We used in the study ammonium polyphosphate of type II CF-APP201 (Shifang Changfeng Chemical Co., Ltd., China), micronized pentaerythrite of RN-P brand and melamine RN-M 40 (Roshal Group, Russia), copolymer EVA Mowilith 1780 (Clariant, Germany), titanium oxide TiO₂ (Sumykhimprom, Ukraine), cetyltrimethylammonium bromide (PanReac AppliChem, Spain), silver nitrate (Alfa Aesar GmbH & Co KG, Germany).

For the synthesis of organoclays, bentonite clay of Kudrinsky deposit (manufactured by JSC "Benta", Crimean blue clay) was used, which, according to technical documents, contains up to 95–98 % of MMT and is characterized by the absence of sandy impurities. The existence of impurities in the clays was controlled by the IR spectroscopy on the IR Fourier spectrometer BX-11 Spectrum (Perkin Elmer, USA). Dimensions, shape and microstructure of the obtained samples were examined using the scanning electron microscope JSM-6490 LV (JEOL, Japan).

4.2. Modification of Na-MMT with silver nitrate

In a flask with a 300-ml capacity, 5 g of Na-MMT were dispersed in 100 ml of the distilled water at room temperature, and then 50 ml of a 10-% solution of silver nitrate were added and agitated in the magnetic stirrer for 3 hours. Clay suspension was kept at room temperature for 1 day, then it was decanted and the sediment was filtered. Upon completion of the process, the resulting material was washed in order to remove the excess of silver nitrate to $pH\approx5-6$ and

dried at a temperature of 20-40 °C. We obtained 3.80 g of clay, modified with silver (Ag-MMT).

4.3. Modification of Na-MMT with polyhexamethyleneguanidine chloride

In a flask with a 500-ml capacity, 5 g of Na-MMT were dispersed in 200 ml of the distilled water at room temperature for 30 min. Next, 4 g of polyhexamethyleneguanidine (PHMG) chloride were added to the resulting suspension in the form of a 50-% aqueous solution and agitated for 5 hours at a temperature of 80 °C. The sediment of montmorillonite, modified with PHMG cation (PHMG-MMT), was filtered, washed with distilled water by decantation three times and dried at room temperature. We obtained 5.1 g of organoclay PHMG-MMT.

4. 4. Modification of Na-MMT with cetyltrimethylammonium bromide

In a flask with a 500-ml capacity, 10 g of Na-MMT were dispersed in 200 ml of the distilled water at room temperature. Next, 200 ml of 0.05 M solution of cetyltrimethylammonium bromide in hot water were added. The mixture was agitated by the magnetic stirrer for 3 hours at a temperature of 50-60 °C. Clay suspension was kept at room temperature for 1 day and decanted; the sediment was filtered, washed with distilled water and centrifuged. It was dried at a temperature of 60 °C for two days until reaching constant weight. 10.7 g of montmorillonite, modified with CTA (CTA-MMT), were obtained.

4.5. Preparation of intumescent composition

Components of the intumescent system (ammonium polyphosphate, pentaerythrite, melamine) at the ratio of (3:1:1), respectively, were placed in a laboratory bead mill. Next, the required amount of admixtures and titanium oxide was added to the mixture. Lastly, 25 % of water of the weight of solid components was added. The mixture was agitated for 30 minutes and separated from the beads. Water dispersion of the polymer or nanocomposite was added to the resulting paste and agitated using a mixer at speed not exceeding 200 rev/min. The finished intumescent composition was used for further studies.

4.6. Fire tests

The prepared intumescent compositions (paints) with the help of a brush were applied to wooden blocks, prepared according in line with GOST 16363-98. Preliminarily dried and weighed samples of wood with coatings were fixed on a device for determining fire-retardant effectiveness according to GOST 16363-98.

4.7. Determining the effectiveness of intumescent paints against wood-staining and mold fungi

The following types of micromycetes were used as the test-organisms: Aspergillus terreus, Aspergillus niger, Penicillium chrysogenum, Paecilomyces variotti Trichosporium, cheteromorphum, Aspergillus hennebergii, Aspergillus flavus, Penicillium cyclopium, and Penicillium purpurogenum. Prepared samples of wood are placed in an exsiccator and kept for 15 days. Condition of the samples is estimated visually. During current assessment of condition of the samples, the average area (%) of damage of their surfaces by fungi is taken into account. When the testing is over, the stage of fungi development (in points) is additionally assessed. The average area of damage of the samples by fungi is defined as the ratio of the sum of areas, damaged by fungi, to the total area of the samples. Assessment of the stage of fungi development on the samples is carried out by a six-point scale according to GOST 30028.4.

5. Results of examining physical-chemical indicators, resistance to biodamage and fire-retardant efficiency

5. 1. Physical-chemical properties of the modified nanoclays

Quaternary ammonium cations – cetyltrimethylammonium (CTA) and cation of polyhexamethyleneguanidine (PHMG), as well as silver (Ag) cations, were used as the modifiers of MMT.

Quaternary ammonium cations were selected as modifiers of MMT to solve the problem of increasing the interlayer spaces and hydrophobization of silicate surface in order to provide its compatibility with polymer molecules of IC. In addition, organomodification of MMT increases the degree of separation of silicate plates and separating them from one another. It creates conditions for the structuring and improvement of rheological properties of intumescent paint. Thus, the coatings with a nanostructured surface, resistant to moisture and environmental conditions, are formed.

The dual character of guanidine compound (as an effective biocide and fireproofing compound) should provide the IC with antibacterial properties and additional indicators of fire-retardant efficiency.

The procedure of obtaining organomodified derivatives of MMT from natural bentonite clay includes two main stages:

1) enrichment of clay for the purpose of extraction of MMT in the form of Na-modified form (Na-MMT);

2) organomodification of Na-MMT with organic compounds (or ions of Ag).

Conversion of bentonite clay into Na-MMT is necessary because Na⁺ ions are characterized by steric compatibility with the surface of layered aluminosilicates. Na⁺ ions do not form such large hydrate shells as ions of Li⁺, Mg²⁺ and $Ca^{\scriptscriptstyle 2+}\!\!\!\!$. It is known that cations of $Ca^{\scriptscriptstyle 2+}$ and $Mg^{\scriptscriptstyle 2+}$ increase interlayer distances in MMT by additional 3 Å compared to Na-form of MMT. However, interaction of polar clays Ca- or Ca-Mg forms even with the polar oligomers and polymers is sterically difficult. Dispersion of Ca-Mg-forms of MMT is ineffective and does not lead to noticeable intercalation of organic molecules in the interlayer spaces of aluminosilicate. A significant decrease in the degree of exfoliation of silicate particles in the polymer matrix is also observed. That is why conversion of bentonite clay into the sodium form is very important from the standpoint of the overall technology of obtaining MMT of high degree of purity. This to some extent applies to receiving organoclays, nanocomposites and composite mixtures.

For the identification of Na-modified MMT, which was subsequently used as a source raw material for obtaining organomodified MMT, the method of IR spectroscopy was applied. This method is sensitive to the character of layered silicates, as well as to the contents of octahedral atoms (Al, Fe, Mg) in the structure of an analyzed substance, and respectively to the changes that occur at different stages of processing of minerals. In the analysis of the infrared spectra of natural and modified bentonites, the two main areas are

separated. In the region of $4000-3000 \text{ cm}^{-1}$, there exist the bands of valence fluctuations of OH-groups that belong to octahedral cations, as well as water molecules, associated with hydrogen bonds. In the region of 1400-400 cm⁻¹, the bands of absorption of the structure of silica clay are concentrated. IR-analysis of the organomodified MMT is described in detail in [10]. It follows from the IR spectra that in the modified clay there was a decrease in the intensity of transmission at a frequency of 3650-3635 cm⁻¹, associated with an increase of hydroxyl groups in the samples. Such a change in the intensity of the band most likely means an increase in exchange capacity of the modified clay compared to the original. This is a consequence of increasing inter-layer distances (d, nm) of organomodified natural silicate. The values of d, calculated by the Wulff-Bragg's formula with the involvement of data of X-ray phase analysis of modified nanoclays, are given in Table 2.

Table 2

Interlayer distances (d, nm) and the content of organic component (%) in modified montmorillonites

Cation	d, nm	%
Na	1.19	7.24
СТА	1.95	33.2
PHMG	2.06	35.4
Ag	1.42	7.75

The content of organic component in the organomodified MMT was calculated according to data of element analysis on determining the carbon content in samples. It should be noted that such method of calculating an amount of modifier does not provide information in what way the organic molecules are located in the structure of clay – whether they are intercalated to the matrix of aluminosilicate or sorbed on the surface. However, it makes it possible to determine the amount of the organic compound, which makes up 33–35 % (Table 2) of the total weight of MMT.

In order to obtain montmorillonite, modified with silver (Ag-MMT), sodium clay was treated with an aqueous solution of silver nitrate. According to X-ray fluorescence analysis, the product of modification contains 7.75 % of Ag and practically does not contain Na⁺ cations, which indicates quantitative progress of the cationic exchange.

5. 2. Biocidic activity of montmorillonite with cations of silver and guanidine in the composition of intumescent coating

To determine effectiveness of intumescent paints relative to mold and wood-staining fungi according to GOST 30028.4, we prepared IC, the composition of which is given in Table 3.

Prepared compositions IC-I–IC-V were applied to the wooden blocks in order to determine their effectiveness against wood-staining and mold fungi. After 15 days of exposure, we carried out assessment by the magnitude of average area of samples (%), affected by fungi, and by the stage of a fungus development. The latter was assessed by a five-point system:

0 – absolutely clean samples at visual inspection and under a microscope;

1 – samples are clean visually; under a microscope, it is possible to see a slight damage in the form of spots of one species of fungi; the stage of spore-bearing is missing; 2 – surface development of mycelium of certain kinds of fungi in the form of spots, spore-bearing stage is missing;

3 – abundant growth of mycelium of certain kinds of fungi, beginning of the stage of spore-bearing of one type of fungi;

4 – clearly visible growth of fungi during visual inspection, various stages of spore-bearing in most kinds of fungi;

5 – deep damage by fungi over the entire area of the sample, intensive spore-bearing.

Table 4 gives results of assessment of effectiveness of paints against mold and wood-staining fungi.

Table 3

Formulation of intumescent compositions

No.	Sample cipher	Base	Organoclay	
1	IC-I	$APP/PE/MA/EVA/TiO_2$	-	
2	IC-II	APP/PE/MA/EVA/TiO ₂	СТА-ММТ, 2 %	
3	IC-III	APP/PE/MA/EVA/TiO ₂	PHMG-MMT, 2 %	
4	IC-IV	APP/PE/MA/EVA/TiO ₂	Ag-MMT, 2 %	
5	IC-V	APP/PE/MA/EVA/TiO ₂	Ag-MMT+ +PHMG-MMT, (1+1) % %	

Table 4

Results of assessment of effectiveness of paints against mold and wood-staining fungi

No.	Sample cipher	Physical a ppearance	Area of damage, %	Stage of fungus de- velopment, points
1	IC-I		Larger than 50	3–5 non-effective
2	IC-II		Larger than 50	3–5 non-effective
3	IC-III		10-30	1–2 effective
4	IC-IV		10-30	1–2 effective
5	IC-V		0-10	0–1 highly effective

Dependence of degree of fire protection of intumescent compositions on the admixtures of organoclays after testing for resistance to biodamage was demonstrated by the method of testing of fire-protection efficiency according to GOST 16363-98. Results of tests of fire protection efficiency are given in Table 5.

An increase in the weight loss of samples after testing is expected to be proportional to the degree of biodamage of the coating. Maximum decrease in the fire protection efficiency is characteristic of IC-I sample, in the coating of which there are no admixtures of nanoclay. In contrast to this, the highest fire protection efficiency was demonstrated

by IC-V sample, the coating of which contains admixture of Ag-MMT+PHMG-MMT.

Weight loss of samples after testing by a method of ceramic pipe

Table 5

Table 6

No.	Sample cipher	Weight loss, %			
		Reference samples	Samples after biodamage testing		
1	IC-I	8.5	11.2		
2	IC-II	6.8	9.4		
3	IC-III	5.3	8.2		
4	IC-IV	5.9	7.4		
5	IC-V	6.4	8.0		

5. 3. Field fire tests of intumescent paints

Dependence of a degree of fire protection of wood by intumescent paints on the admixtures of nanoclay was demonstrated by the method of testing fire protection efficiency according to GOST 16363-98. Composition of the finished fire-retardant paints based on IC-I (APP/PE/MA/ EVA) and those with the admixtures of nanoclays is given in Table 6. We used organoclays Na-MMT, CTA-MMT, PHMG-MMT and Ag-MMT as the admixtures.

Composition of fire-retardant paints for wood

Component	Content of component in the system, % by weight					
I I I I I I	1	2	3	4	5	
APP	20	20	20	20	20	
MA	10	10	10	10	10	
PE	10	10	10	10	10	
EVA	15	20	20	20	20	
TiO ₂	10	10	10	10	10	
Water	35	33	33	33	33	
Na-MMT	_	-	-	-	-	
CTA-MMT (method a)	_	2	_	_	_	
CTA-MMT (method b)	_	_	2	_	_	
PHMG-MMT	—	-	_	2	-	
PHMG-MMT+ +Ag-MMT	_	_	_	_	2	
Max. T of flue gases, °C	224	205	200	208	210	
Average weight loss, %	8.5	5.3	4.8	5.9	6.4	
Group of fire retardant effectiveness	Ι	Ι	Ι	Ι	Ι	
Viscosity, Pa·s	7.03	12.3	14.2	11.9	10.8	

Intumescent paints were prepared in two ways:

a) clay was mixed equally to other solid ingredients;

b) clay in the required amount was pre-mixed for 2 hours with the dispersion of EVA to receive the intercalated nano-composite.

6. Discussion of results of examining the effect of nanoclays on resistance to biodamage and fire protection efficiency of intumescent coatings

Comparison of physical appearance of samples IC-I–IC-V (Table 4) makes it possible to state that biocidic admixtures of PHMG-MMT and Ag-MMT increase the stability of fire retardant paint with composition of APP/PE/MA/EVA/TiO₂ against mold and wood-staining fungi of the examined strain. It is essential that the mixture of nanoclays PHMG-MMT+ +Ag-MMT, tested in concentrations (1+1) % in accordance with GOST-30028.4, demonstrates the synergic effect. This composition belongs to highly effective antiseptics that can be used to protect wood against blue stain and mold fungi.

Results of fire testing of IC-I–IC-V (Table 5), as it was expected, showed an increase in the weight loss of samples in proportion to the degree of biodamage. The most significant decrease in fire protection efficiency with the loss of group I is observed for sample IC-I, which does not contain any admixtures of nanoclay. The lowest weight loss after the impact of a ceramic tube is characteristic for sample IC-V, the coating of which is classified as highly effective against mold and wood-staining fungi.

It should be noted that in Ukraine it is allowed to apply for fire protection only the agents that provide fire protection efficiency of group I.

An analysis of data on testing of fire protection efficiency of paints IC-I-IC-V according to GOST 16363-98 (Table 6) shows, first, a slight effect of admixtures of nanoclay in the system APP/PE/MA/EVA and, second, a relatively low sensitivity of the examined system to the structure of the admixture. If we compare temperature values of outgoing gases, which are observed in the case of existence of clay Na-MMT (No. 2, Table 6) or organomodified clay CTA-MMT (No. 3, 4, Table 6) in the system, it is possible to observe a slight decrease in temperature from 224 °C for the unadulterated IC-I (No. 1, Table 6) to 205 °C for the systems containing CTA-MMT (No. 3, 4, Table 6). However, admixtures of nanoclays into water-based intumescent paints for wood are able, as it was shown earlier, to prolong the term of operation of a coating [10]. When using nanoclays with antibacterial properties (in particular PHMG-MMT, Ag-MMT or a mixture), it is possible to enhance resistance to biodamage. In addition, admixtures of nanoclays with antibacterial properties contribute to an increase in viscosity of the paint (Table 6) and may be used as an effective thickening agent.

It was demonstrated previously [2] that the existence of ions of nanosilver and polyhexamethyleneguanidine derivatives in the paint "Evafarb" provides the coating with a wide range of biocidic effect: bactericidal, virulicidal, fungicidal, sporocidal and algicidal. Data on the antibacterial properties of the coating "Evafarb", which were examined in accordance with the national standards and techniques, are given in Table 7.

According to the conclusion of microbiological research, the paint that contains the mixture of cations of Ag⁺ and PHMG⁺ is characterized by the disinfectant action relative to gram-positive and gram-negative bacteria, as well as to mold fungi. That is why the use of fire-retardant intumescent paints with such composition could be part of the disinfection measures in public places, medical organizations, and pharmaceutical enterprises.

	artificial contamination with test-strains							
	Object of	Effectiveness of disinfection after 24 hours/30 days						
	disinfection	S. aureus	E. coli	C.albicans	A. niger	M /tuberculosis B_5		
ſ	Wood	90.4/97.0	92.2/99.2	94.5/99.5	91.2/91.2	100/100		
	Gypsum-board	93.1/91.0	90.5/99.4	90.5/95.0	91.5/93.5	100/100		
	Concrete	90.0/93.9	91.5/97.0	89.9/91.0	90.5/95.5	98.7/100		

Effectiveness of disinfection of objects, treated with the paint "Evafarb" at artificial contamination with test-strains

7. Conclusions

1. We determined resistance of intumescent coatings composed of ammonium polyphosphate/pentaerythrite/ melamine/EVA/titanium oxide with admixtures of montmorillonite, modified with guanidine and quaternary ammonium cations, as well as ions of silver, in relation to mold and wood-staining fungi. It was shown that the use of montmorillonite modified with ions of silver and guanidine cation improves the class of biocidal effectiveness of a coating from "not effective" to "effective". It was found that the mixture of Ag-montmorillonite and PHMG-montmorillonite demonstrates synergistic effect against mold and wood-staining fungi and provides the "highly effective" class of biocidal effectiveness of the coating. 2. We conducted field fire tests of intumescent paints for wood composed of ammonium polyphosphate/pentaerythrite/melamine/ copolymer EVA/titanium oxide containing Na-MMT, CTA-MMT, PHMG-MMT and Ag-MMT, according to GOST 16363. It was shown that the admixtures of nanoclays in water-based intumescent paints decrease the temperature of flue gases and transfer wood into group I of fire-protection effectiveness.

Results of present research allow us to recommend including the mixture (PHMG-MMT+Ag-MMT) into the formulation of intumescent paints as effective antibacterial admixtures, which have disinfectant effect in relation to the gram-positive and gram-negative bacteria as well as mold fungi.

Acknowledgement

Present article reports results of research, carried out under the grant support of the State Fund of Fundamental Research by the contest project F-71 for scientific and scientific-technical projects of academic institutions and higher educational establishments in the Crimea and temporarily occupied territories that are currently based at other national institutions.

References

- Regulation (EU) No 305/2011 of the European Parliament and of the Council laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC [Electronic resource]. – Available at: http://eur-lex.europa.eu/ legal-content/EN/TXT/?uri=celex%3A32011R0305
- Vahitova, L. N. Novye materialy v stroitel'stve. Antimikrobnye LKM v Ukraine [Text] / L. N. Vahitova, M. P. Lapushkin // Budivnytstvo Ukrainy. – 2013. – Issue 3. – P. 8–11.
- Pat. No. US 20080161268 A1. Quaternary ammonium salt antibacterial and water-borne coating material having antibiotic property containing the same [Text] / Yen C-L., Tien P., Huang Y.-C., Huang C. H.; Compal Electronics, Inc. – No. US 11/829,085; declareted: 27.07.2007; published: 03.07.2008.
- Xue, Y. Antimicrobial Polymeric Materials with Quaternary Ammonium and Phosphonium Salts [Text] / Y. Xue, H. Xiao, Y. Zhang // International Journal of Molecular Sciences. – 2015. – Vol. 16, Issue 2. – P. 3626–3655. doi: 10.3390/ijms16023626
- Ng, V. W. L. Antimicrobial Polycarbonates: Investigating the Impact of Nitrogen-Containing Heterocycles as Quaternizing Agents [Text] / V. W. L. Ng, J. P. K. Tan, J. Leong, Z. X. Voo, J. L. Hedrick, Y. Y. Yang // Macromolecules. – 2014. – Vol. 47, Issue 4. – P. 1285–1291. doi: 10.1021/ma402641p
- Peyre, J. Co-Grafting of Amino–Poly(ethylene glycol) and Magainin I on a TiO2Surface: Tests of Antifouling and Antibacterial Activities [Text] / J. Peyre, V. Humblot, C. Methivier, J.-M. Berjeaud, C.-M. Pradier // The Journal of Physical Chemistry B. – 2012. – Vol. 113, Issue 47. – P. 13839–13847. doi: 10.1021/jp305597y
- Bagheri, M. Mode of Action of Cationic Antimicrobial Peptides Defines the Tethering Position and the Efficacy of Biocidal Surfaces [Text] / M. Bagheri, M. Beyermann, M. Dathe // Bioconjugate Chemistry. – 2012. – Vol. 23, Issue 1. – P. 66–74. doi: 10.1021/ bc200367f
- Hajipour, M. J. Antibacterial properties of nanoparticles [Text] / M. J. Hajipour, K. M. Fromm, A. Akbar Ashkarran, D. Jimenez de Aberasturi, I. R. de Larramendi, T. Rojo et. al. // Trends in Biotechnology. – 2012. – Vol. 30, Issue 10. – P. 499–511. doi: 10.1016/ j.tibtech.2012.10.007
- Bahar, A. Antimicrobial Peptides [Text] / A. Bahar, D. Ren // Pharmaceuticals. 2013. Vol. 6, Issue 12. P. 1543–1575. doi: 10.3390/ph6121543
- Vakhitova, L. The effect of organoclays on the fire-proof efficiency of intumescent coatings [Text] / L. Vakhitova, V. Drizhd, N. Taran, K. Kalafat, V. Bessarabov // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 6, Issue 10 (84). – P. 10–16. doi: 10.15587/1729-4061.2016.84391
- Wang, J. The protective effects and aging process of the topcoat of intumescent fire-retardant coatings applied to steel structures [Text] / J. Wang // Journal of Coatings Technology and Research. – 2015. – Vol. 13, Issue 1. – P. 143–157. doi: 10.1007/s11998-015-9733-9
- 12. Mariappan, T. Recent developments of intumescent fire protection coatings for structural steel: A review [Text] / T. Mariappan // Journal of Fire Sciences. 2016. Vol. 34, Issue 2. P. 120–163. doi: 10.1177/0734904115626720
- Puri, R. G. Intumescent coatings: A review on recent progress [Text] / R. G. Puri, A. S. Khanna // Journal of Coatings Technology and Research. – 2016. – Vol. 14, Issue 1. – P. 1–20. doi: 10.1007/s11998-016-9815-3

Table 7