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THE ENVIRONMENTAL IMPACT REDUCTION PRINCIPLES OF BIOPROTECTIVE PAINTWORK MATERIAL DURING THE WOOD SURFACE PAINT

A bioprotective paintwork materialfor wood surface with reduced content ofbiocide additive has been developed. The fungi inertness of acrilyc, styrene-acrylic and vinyl-acetate-ethylene films on the base of its dispersions has been investigated. It has been shown that the most stable film to the mold fungi when the changing of mechanical properties and chemical structure is a film on the base of acrylic dispertion. The influence of pigments, their volume concentrationand paint surface on the coatingfungi inertness coatingwas studied. It was noticed that zinc oxide among zinc pigment decelerates fungi growthbetter than others. The main principles ofenvironmental impact reduction of abioprotective paintwork material have been defined. They are: the choice a biostable film binder, fungitoxic pigment and inert filler use, their quantities are defined on the pigment volume concentration, except the component which can stimulate fungi growth.

Key words: biostability, fungi inertness, mold fungi, binder, pigment, filler, pigment volume concentration, surface.

Introduction. Today, no construction project cannot do without the use of paintwork materials for different purposes. Special attention is given to security requirements and the protection of the environment. On the one hand, the reduction of emissions of harmful substances into the atmosphere is carried out in the manufacture of paintwork products by optimization of the technological process, on the other, by introduction of new paintwork materials that meet modern requirements. Promising materials with environmenttal, technological and economic points of view, are water-dispersion paintwork compositions. Their main advantage is the use of water instead of expensive, flammable, toxic and irreversibly losing organic solvents. They also have no odor, dry quickly, they are easy to apply to the surface, have good decorative appearance and a wide range of colors. The absence in the composition of the aqueous material of organic solvents significantly reduces the amount of harmful emissions into the atmosphere, reduces flammability, toxicity and creates favorable conditions of work when carrying out painting works [1].

Wood is one of the widely used in construction materials. Each wooden surface needs reliable protection to avoid destruction under the action of external factors. Damage with various microorganisms, in particular fungi, remains a major problem in its exploitation. To prevent the occurrence of bio-corrosion of wood is much easier than to deal with its consequences. The idea of adding in paint special materials and biocide inhibiting additives was implemented in practice long ago [2]. Paintwork material is a complex multi-component system, therefore, it's necessary to consider the specific features of each composition, which may have a significant impact on the stability of the active substances of biocide (temperature and pH of the system; reducing and oxidizing components of the composition; the substrate material; drying temperature of paintwork material; the operating conditions of the coating). In addition, the drugs used as additives to protect against bio-corrosion, need to be not only effective but also safe to use and have no adverse impact on the environment. Lowering of the undesirable effect of biocides can be achieved by reducing their amount in the composition. However, in this case their efficacy against microorganisms will also be reduced. To solve the problem it is proposed by optimization of the formulation to increase the biological stability and give fungi toxicity properties to paintwork materials, and reduce the number of antimicrobial agents in the composition, thereby reducing the environmental burden of bioprotective paintwork material. Thus, the main goal of this work is to optimize the basic formulation, based on biostability and fungi toxicity its components. [1].

Main part. Each component of the paint composition being exposed to metabolites of fungi possesses various biological stability (some destruct quickly, others change the structure less or slightly). On the other hand, there is the response – all of the products included in the composition of the material can influence the growth and development of fungi: to stimulate their growth in the case of being a power source; inhibit or remain inert.

The impact of fungi is primarily the effect of chemically active corrosive medium, secreted by them [3]. In the paintwork coating the film binder is badly affected to a large extend.

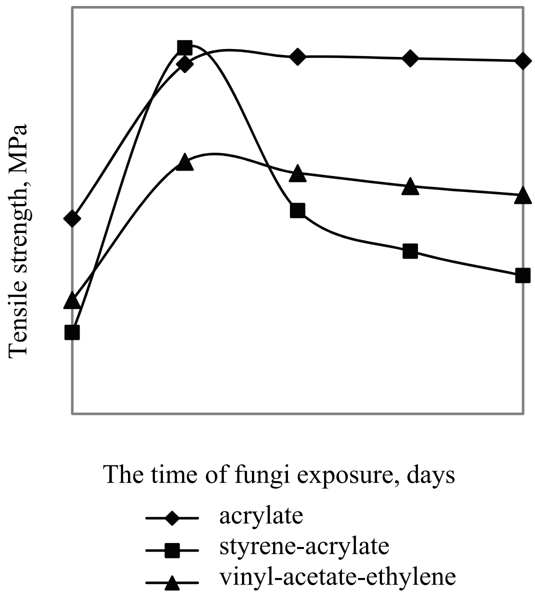

Fig. 1. The dependence of the tensile strength of binders from exposure time fungi

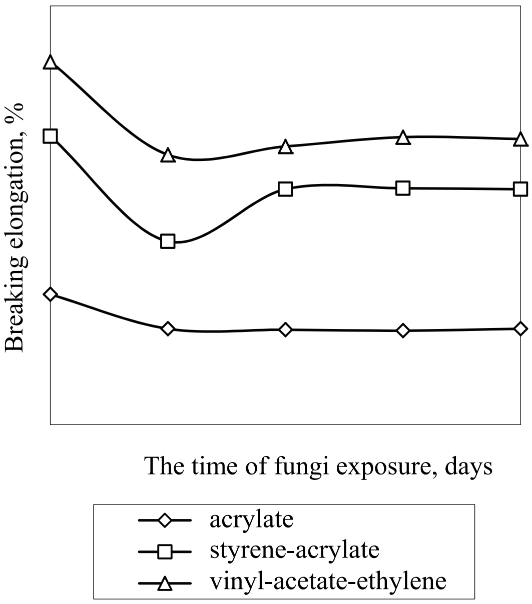

Fig. 2. The dependence of the elongation of binders of fungi exposure time

On exposure of aggressive mediums on polymeric materials macromolecules can undergo the following transformations: a decrease in the degree of polymerization as a result of the collapse of the main chain of the macromolecules in the polymer; cleavage of the molecule of the monomer from the end of the chain of the macromolecule – depolymerization; formation of new chemical bonds between macromolecules, i. d., the reaction of crosslinking [4].

Chemical resistance of polymeric materials can be estimated by the change of their physico-mechanical properties. The consequence of intermolecular interactions is the change of the tensile strength and elongation at break. To study changes in the strength characteristics in a binder-forming substances under the influence of fungi free films produced based on acrylic, styrene-acrylic and vinyl-acetate-ethylene dispersions, were exposed to fungi for rapid methods "agar grid" using fungi Aspergillusniger, Penicillium Funiculosum, Trichodermaviride [5]. It should be noted that the films obtained dispersions have the same assessment of the fungi resistance in accordance with GOST 9.050.

The results of the tests are presented in Fig. 1 and 2, they showed that, after 7 days the tensile strength of the acrylic film increases from 0.24 to 0.43 MPa, styrene-acrylic – from 0.10 to 0.45 MPa, a vinyl acetate-ethylene – from 0.14 to 0.32 MPa.

The elongation is reduced from 140 to 103, from 310 to 197, from 390 to 290% respectively. After 14 days and further exposure to fungi tensile strength is significantly reduced (0.25 MPa) and percentage elongation is increased (up 253%) in styrene-acrylic, to a lesser extent (to 0.30 MPa and 299%) in vinyl acetate-ethylene model slightly (to 0.44 MPa and 102%) of acrylic binders.

It is known [6] that under the influence of corrosive mediums on polymeric materials new chemical bonds between macromolecules can form. Judging by the nature of the changes the strength characteristics of the films we have got the formation of such ties took place. To confirm this assumption was tested by determining the content of the Sol-gel-fraction in the films of the binder without aging and after 7 and 14 days of exposure to fungi (Table 1). Film-forming substance was extracted with benzene for 3 h. The data presented in Table 1, are correlated with previously obtained.

Table 1

The gel-fraction of unpigmented films

Binder	The time of fungi exposure, days	Gel, %
Acrylic	0	70.29
	7	80.12
	14	74.71
	56	72.14
Styrene-acrylic	0	0
	7	71.12
	14	0
Vinyl-acetate-ethylene	0	0
	7	72.98
	14	69.74
	56	1.13

Styrene-acrylic and vinyl-acetate-ethylene binders are not network polymers, so they have no gel fraction. After 7 days of exposure to microorganisms gel fraction of the acrylic film increases to 10%, non-cross-linked styrene-acrylic and vinyl-acetate-ethylene films appear gel-fraction, which is 71.12 and 72.98%, respectively. The data indicate that, under the action of fungi in the macromolecular film-forming substances, the formation of new cross chemical bonds is hold due to recombination of macroradicals. When microorganisms affected more than 7 days gel-fraction of all films was decreased.

Thus, acrylic dispersion was selected as film-forming in the bioprotective paintwork composition, which is the least susceptible to change the deformation and strength properties after 7 days of exposure to fungi.

The next step in the development of bioprotective material is a selection of pigments and fillers. By choice of pigment for paintwork material, we usually do not consider its effects on the microbiological resistance of the resulting protective coating. Meanwhile the role of this component of coatings to ensure their biostability has significant value in composition of some materials. Pigments can mechanically inhibit the development of mycelium, exert a toxic action on microorganisms, including fungi.

According to the scale of production and use in paintwork materials, white pigments occupy the first place, they constitute 65–70% of the total weight of the produced pigments.

From a large number of inorganic substances of white color as the pigments are applied only few technical products that meet the complex physical, chemical, technical, economic and sanitary-hygienic requirements. They include: titanium dioxide, oxide and Sulfide of zinc, lithopone. The literature route proved [1, 7] that oxide and zinc sulfide, lithopone have fungitoxic properties.

Comparative evaluation of resistance to fungi zinc-containing pigments in the composition model compositions based on acrylic, styrene-acrylic and vinyl-acetate-ethylene dispersions was obtained (Fig. 3). It is established that titanium dioxide hasn't significant influence on the inhibitory ability of the coatings (increased duration of the lag phase of the fungus for 1 day). Most fungitoxicity with a water-dispersible film formers zinc oxide showed. Spores remained without visible changes throughout the test period on all surfaces. Films containing lithopone and zinc sulfide did not possess antifungal properties, which is associated with a lower content of zinc ions in the pigments (lithopone contains 20% of zinc, sulfide of zinc – 67.1%, and zinc oxide – 80%), and therefore in the paintwork composition (the amount of zinc in coating with zinc oxide was 24%, the zinc sulfide – of 20.13%, lithopone – 6%).

Thus, fungitoxic properties of the coatings were determined mainly by the pigments, as well as the lag-phase of all films containing the same pigment was the same. The best bioprotective properties in the composition of models zinc oxide had.

Fillers, the active components of pigmented paintwork materials, are applied to optimize the formulation and improve the technical properties of the paintwork material and coating. Compared with the pigments fillers reduced bioprotective properties of coatings, or had no effect on fungitoxicity of the film. This is due to the fact that the metals included in the composition of fillers, are not toxic to the microorganisms, in addition, some fillers can increase the hygroscopicity of the coating, thereby contribute to the intensivedevelopment of microorganisms development of microorganisms.

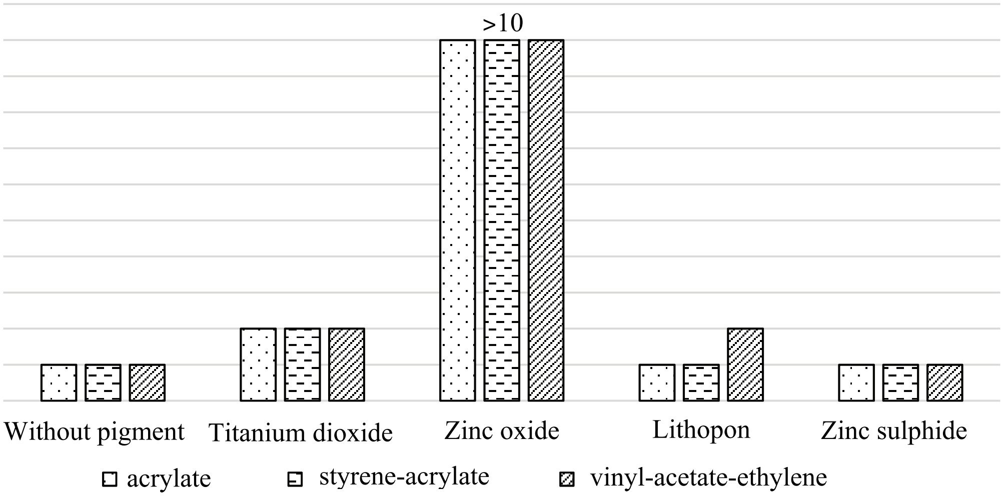

Fig. 3. The duration of the lag phase (days) A. on the films containing pigments

Thus, for the further development of the paintwork material inert to fungi titanium dioxide was selected for giving the covering power, zinc oxide to increase fungitoxicity and calcite to reduce the cost of paint, and also to control certain technical characteristics [7].

In addition, the composition of the paint consisted of: a dispersant (sodium of polycarboxylic acid), antifoam (a mixture of hydrophobic solids and polysilazane in polyglycol), nonionic associative thickeners based on polyurethanes (since the use of cellulosic thickeners stimulates the growth of micromycetes), coalescent (2,2,4-trimethyl-1,3-pentacyanonitrosylferrate).

The planning of the experiment was carried out with the help of the simplex-lattice plans of Sheffe for three-component simplex [8].

It is known that bioprotective properties of the coatings are significantly affected by the surface. Therefore, the amount of pigment and filler were selected so as to minimize the influence of wood surface. The pigment of the composition was 35 wt %. The ratio of pigments and fillers calculated on the basis of restrictions in local regions of the factor space with regard to volume concentration of pigments in a given area was maximum. In Table 2 the numbers of compositions and ratios of components of the pigment part are presented (wt %).

Table 2

Structure of pigmented part of the compositions, %

Number of composition	Dioxide titanium	Zinc oxide	Calcite	VPC , %
1	15.00	15.00	5.00	38.0
2	16.65	15.00	3.35	37.4
3	18.35	15.00	1.65	36.8
4	20.00	15.00	0	36.1
5	16.70	16.65	1.65	36.4
6	13.30	18.35	3.35	36.7
7	10.00	20.00	5.00	37.0
8	11.65	18.35	5.00	37.4
9	13.35	16.65	5.00	37.7
10	15.00	16.65	3.35	37.1

The largest value of the volume concentration of pigment was observed in composition No. 1. Table 3 shows the results of tests on fungal resistance of the resulting compositions.

The study was carried out according to GOST 9.050 using method 1 (without additional power supply) and 2 (in the presence of the power source) in the form of free films, and also on a wooden surface (on a 6-point scale from 0 to 5; scores 0 and 1 – the coating has bioprotective properties).

It was found that without substrate all formulations had the same fungus resistance. When painting wood surfaces the best biostability (0 points according to method 1; 2 points according method 2) the composition No. 1 had, volume concentration of pigment in which was the highest and amounted to 38.0 %.

Table 3

Funginertness according to GOST 9.050 methods 1 and 2 coatings in the form of free film and on wooden surface

Number of composition	Free film		On substrate		VPC , %
	1	2	1	2	
1	0	2	0	2	38.0
2	0	2	1	3	37.4
3	0	2	1	3	36.8
4	0	2	1	3	36.1
5	0	2	1	3	36.4
6	0	2	1	3	36.7
7	0	2	1	3	37.0
8	0	2	1	3	37.4
9	0	2	1	3	37.7
10	0	2	1	3	37.1

Thus, with equal fullness the best bioprotective properties of wood a composition with a higher volume concentration of pigment had. When the value of RWT is high it creates a barrier effect, thereby reducing the effect of the painted surface.

Among the compounds characterized by high activity in combination with relatively low toxicity to humans, nitrogen-containing heterocyclic compounds are contained, in particular isothiazolinone. They, unlike other biocides, are stable in alkaline medium, do not cause color change of paint material, are halogen-free. As biocidal additives, isothiazoline sold under the trademark ActicideDW was introduced. To determine the concentration of biocide at which the coating will completely inhibit the growth of fungi, the composition was injected additive in an amount of 0.01 wt % with a step of 0.002 (Fig. 4).

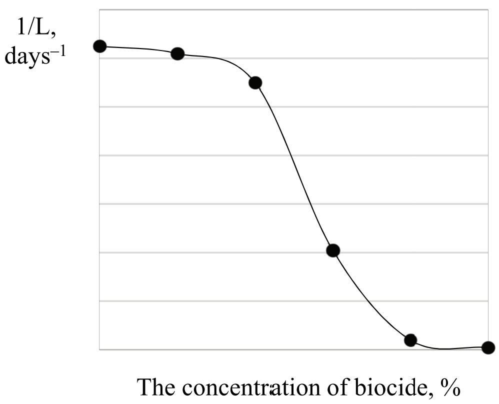

Fig. 4. The effect of biocide of isothiazolinones on fungitoxicity paintwork, defined by method "agargrid"

Table 4

Technical characteristics of the developed paintwork material

Characteristic	Value
Weight percent, %, not less	50
pH	8.5–9.1
Drying time to degree 3 at temperature (20 ± 2)°C, hour, not more	1
Degree of grinding, mcm, not more	40
Spreading capacity, g/m^2, not more	80
Adhesion, MPa, not less	2
Film resistance to static impact of water at a temperature of (20 ± 2)°C, hour, not less	48
Nominal light-resistance, hour, not less	24
Vapor transmission, mg · m^{-2} · h^{-1} · Pa^{-1}	0.008
Funginertness, GOST 9.050, point (method 1 / method 2)	0 / 1

This figure shows that the coating completely inhibited the growth of fungi when the concentration of biocide is 0.008%. Manufacturer recommended to add from 0.10 to 0.40% biocide. Thus, when painting wood designed composition allowed to reduce the content of biocidal additives at 12.5 times from the recommended amount.

In addition, bioprotective composition must be resistant to the effects of mold fungi, it should also have high technical characteristics.

Table 4 shows the specifications of developed bioprotective paintwork composition. All obtained coatings were dried up to level 3 less than 1 h and gave a film with a uniform matte surface.

Testing of coatings for resistance to the exposure to water was carried out in accordance to GOST 9.403. After 50 h of static exposure to water changes of the external appearance of the coating were not observed. After 24 h of UV irradiation lamp decorative and protective properties of coatings were also unchanged. Adhesion of coatings was 2 MPa.

Thus, the developed bioprotective material with reduced level of biocide had a high value of technical characteristics such as adhesion, hiding power, water resistance, vapor permeability.

Conclusion. Studies have shown the possibility of creating a bioprotective paintwork composition for painting wood surfaces with reduced level of biocide and allowed to formulate the basic principles of reducing environmental load in the development of bioprotective materials: the selection of the most bioresistant film-former; selection of pigments and fillers must occur from the point of view of their activity against mold fungi and their quantity in the composition should be determined taking into account the volume concentration of pigment. For painting of wooden surface volume concentration of pigments should be maximized (at least about 38%) to create a barrier effect, which decreases the influence of wood, as wood is an organic material of natural origin and provides a carbon food source for many living organisms; it is also necessary to exclude the use of components that stimulate the growth and development of fungi.

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