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DEVELOPMENT OF BIOPROTECTIVE PAINTWORK MATERIAL FOR INTERIOR FINISH OVER MINERAL SURFACE

A bioprotective paintwork material has been developed using mineral substrates without biocide additives. The influence of zinc oxide, titanium dioxide and calcium carbonate on such important film characteristics as opacity, vapor permeability and funginertness has been studied. It has been shown that paint surface can influence on the coating funginertness. It has been simulated conditions which allow define coating processes when fungi aggressive environments take place on it.

Introduction. The problem of mold fungi affection of buildings has been widely developing over the latest few years. Fungus spores are everywhere – in air, water, in the surface of the walls and inside them. As soon as spores get into favorable environment they start growing out and affecting external environment in spite of its structure and composition. For a successful fighting with mold fungi it is necessary to establish and eliminate the reason of its appearing and also carry out an antiseptic processing of affected area.

However, it is more effective initially use materials with bioprotective properties. To receive such properties biocide agents are usually added into paintwork materials. Recently, there can be observed a tendency of toughening ecological and medical requirements to paint industry and biocide industry. As a result, usage of a big number of highly effective agents composing paintwork materials are limited or banned. Besides, the similar additives considerably increase price of the product.

As a rule, during the development of formulation of bioprotective paint materials fungitoxicity of the material itself is not taken into account. Many components of the composition can itself influence fungitoxicity of coating. Some of them create favorable conditions for the development of mold fungi and sometimes stimulate their growth while the others can inhibit their microbiological activity. The aim of the present work is studying of mutual influence of pigments in composition on fungitoxicity of coating that will allow developing bioprotective composition with minimal quantity of biocide or without it.

Main part. Earlier studies [1, 2] on fungitoxicity of components of paint composition have allowed to define components for further development of bioprotective material. Acrylic dispersion was used as film-forming agent. Titanium dioxide and zinc oxide pigments were also included into the composition. For cost saving of the paint and also for regulation of some technical characteristics, calcite was introduced into the composition. Planning of the experiment has been carried out with the help of Scheffe's simplex-lattice design for ternary simplex. For the achievement of the condition: total component in every point of factor space is constant and total pigment volume concentration (PVC) 25–40% vol. (for achieving high operational parameters of coating) three factor triangles have been examined in which sum of pigments and filler was 25, 30 and 35 wt % (Fig. 1). In local areas of factor space there were limitations about two components: titanium dioxide 10–20 wt % (for providing of high coverage rate and whiteness of coating) and zinc oxide 5–20 wt % (as part of model composition on basis of chosen dispersion it inhibited growth of fungi in specified limits). The third component – calcite was calculated by subtraction out of the sum of component titanium dioxide and zinc oxide. Triangle ZXV was formed the basis of simplex lattice at the sum of pigments 25 wt %, at 30 wt % – triangle TRV; at 35 wt % – triangle ABC. Coordinates of corners of triangles were recorded with the help of matrices. On the basis of the matrix of borderlocal area and the matrix of experiment in relative units of internal simplex in Mathcad package, the quantity of each component constituting the composition of experimental samples of paintwork materials was calculated in natural units of external simplex.

In table 1 there are numbers of examined compositions and constituents of their pigment part (under the pigment part all pigments and filling agents constituting the composition are understood) in volume terms in grams and also pigment volume concentration.

Besides the pigment part, paintwork compositions included 30 wt % of acrylic dispersion, dispergator – sodium salt of polycarboxylic acid, defoamer – blend of hydrophobic solid substances and foam-destroying polysiloxanes in polyglycol, polyurethanes associative nonionic thickeners, coalescent 2,2,4-trimethyl-1,3-pentadiolmonoisobutirat.

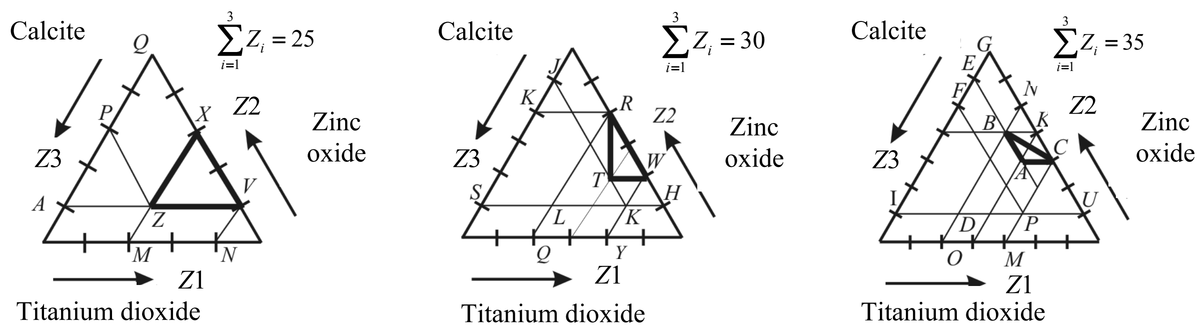

Fig. 1. Singling out of local areas of factor space

Table 1

Compound of a pigment part of the examining compositions, %

Number of compound	Titanium dioxide	Zinc oxide	Calcite	VCP, % v.	Number of compound	Titanium dioxide	Zinc oxide	Calcite	VCP, % v.
1	10.00	5.00	10.00	34.6	16	13.30	16.70	0	31.8
2	13.30	5.00	6.70	33.2	17	10.00	20.00	0	30.9
3	16.70	5.00	3.30	31.7	18	13.30	15.05	1.65	32.9
4	20.00	5.00	0	30.3	19	16.70	9.95	3.35	34.7
5	16.70	8.30	0	29.4	20	16.70	11.65	1.65	33.6
6	13.30	11.70	0	28.5	21	15.00	15.00	5.00	38.0
7	10.00	15.00	0	27.6	22	16.65	15.00	3.35	37.4
8	10.00	11.70	3.30	30.1	23	18.35	15.00	1.65	36.8
9	10.00	8.30	6.70	32.5	24	20.00	15.00	0	36.1
10	13.30	8.30	3.40	34.6	25	16.70	16.65	1.65	36.4
11	15.00	10.00	5.00	35.4	26	13.30	18.35	3.35	36.7
12	16.65	10.00	3.35	34.7	27	10.00	20.00	5.00	37.0
13	18.35	10.00	1.65	34.0	28	11.65	18.35	5.00	37.4
14	20.00	10.00	0	33.3	29	13.35	16.65	5.00	37.7
15	16.70	13.30	0	32.6	30	15.00	16.65	3.35	37.1

All obtained paint films dried to the extent of 3 for the period of time less than 1 hour and provided the film with flat mat surface. Testing of coatings on water resistance has been carried out in conformity with National State Standard NSS 9.403. After 50 hours of static effect of water, changing of external appearance of coatings has not been observed. 24 hours later of lamp UV-exposure, decorative and protective properties of coatings have not been also changed. Adhesion of coatings on mineral surface made 2 MPa.

Opacity is one of the most important properties of paintwork material. Opacity – is a capability of paintwork material hide the color of bottom layer. It is desirably that opacity of the paint will be higher; it will allow to cut material consumption. Opacity depends on differences of refraction indexes of using materials (dispersion, pigments and filling agents): the more the difference the higher the opacity. While revealing of opacity of thirty compositions with pigment part of 25, 30 and 35% mas. it was established that in case of increasing of titanium dioxide opacity of all examining paint films increased (Fig. 2). Zinc oxide decreased opacity and influence of calcite was determined by the content of pigments in a composition. The ability of zinc oxide to effect in a negative way on the examining property, in spite of it has a rather high refraction index (zinc oxide 2.06; titanium dioxide 2.7; calcite 1.59; dispersion 1.5), is connected with the fact that this pigment has a rather low opacity and high density in comparison with titanium dioxide and calcite.

In case of increasing of zinc oxide content in paintwork material increase of mass has been observed, consequently, paint consumption and opacity slightly increased.

Vapor transmissivity is an important factor influencing coating life.Paintwork coating should be vapor-permeable otherwise moisture will accumulate under the paint layer that can lead to early destroying of the coating. If there is no a special task of creation of vaporproof layer on wall surface the paint should have maximal vapor transmissivity. But in practice, other not less important properties of coating are to be taken into consideration and choose sound compromiss between these parameters.

While examining of vapor transmissivity of coatings consisting of 25, 30 and 35 wt % of pigment part it has been established that zinc oxide influenced the most on the examining property: in case of its increase vapor transmissivity has been increasing in all examining compositions. Increase of titanium dioxide in experimental compositions has also had a positive impact on vapor transmissivity of coatings. Increase of filling agent has had a negative impact on the examining property (Fig. 3).

Critical pigment volume concentration (CPVC) of acrylic dispersions for standard pigments and filling agents usually makes 40–60% vol. (in the area of CPVC rheological properties of paintwork materials sharply change and mechanical and protective properties of coatings; for water-dispersion paints CPVC value is often determined by sharp increase of vapor transmissivity coefficient). Vapor transmissivity coefficients in compositions No. 21-30 have more increased than in other compositions. It proves the fact that VPC of coatings No. 21-30 has been reaching the deadline. Thus, in case of further filling of the film vapor transmissivity of coatings will increase but other important properties of bioprotective paintщщкл material will deteriorate. Therefore, it would be unreasonably to carry out studies when pigment part is higher than 35% mas. and volume concentration of pigment is higher than 38% vol.

Funginertness (table 2) of obtained compositions according to NSS 9.050 by methods 1 (under the circumstances excluding additional energy source) and 2 (with the energy source) in a form of unsupported film and also on mineral surface has been studied. Samples of unsupported filler paste were used as a control. Funginertness of mineral surface received 3 scores assessment (on 6-rating scale from 0 to 5; scores 0 and 1 – coating has bioprotective properties).

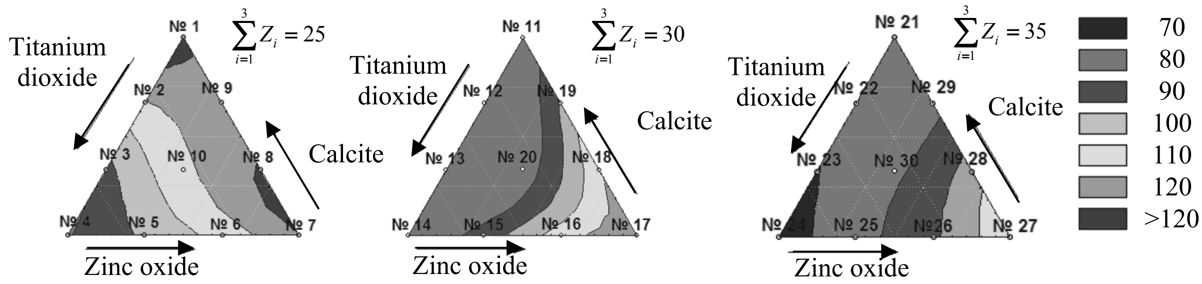

Fig. 2. Opacity of paintwork materials at different content of pigment part, g/m^2

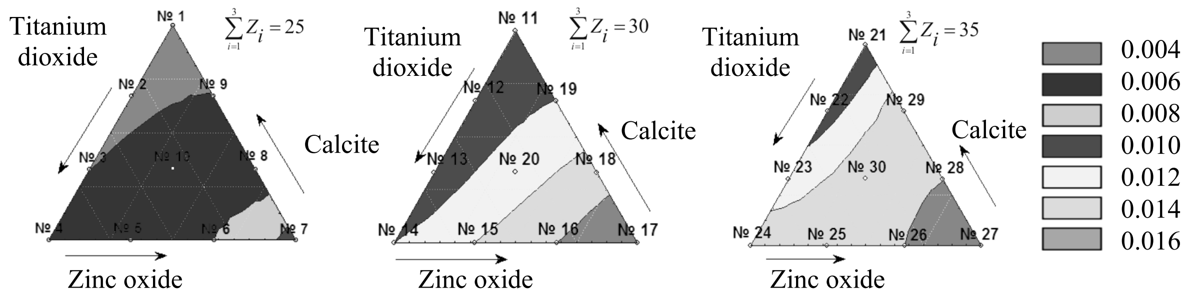

Fig. 3. Vapor transmissivity of coatings at different content of pigment part, mg · m^{-2} · h^{-1} · Pa^{-1}

Table 2

Funginertness according to NSS 9.050 by methods 1 and 2 of paintwork materials in a form of unsupported film and on mineral surface

Number	Unsupported film		Supported film		VPC, % vol.	Number	Unsupported film		Supported film		VPC, % vol.	Number	Unsupported film		Supported film		VPC, % vol.
	1	2	1	2			1	2	1	2			1	2	1	2	
1	1	3	1	2	34.6	11	1	3	1	2	35.4	21	0	2	0	1	38.0
2	1	3	1	2	33.2	12	1	3	0	2	34.7	22	0	2	0	1	37.4
3	1	3	0	2	31.7	13	1	2	0	2	34.0	23	0	2	0	1	36.8
4	1	3	0	2	30.3	14	0	2	0	2	33.3	24	0	2	0	1	36.1
5	1	3	0	2	29.4	15	0	2	0	1	32.6	25	0	2	0	1	36.4
6	1	3	0	2	28.5	16	0	2	0	1	31.8	26	0	2	0	1	36.7
7	0	2	0	1	27.6	17	0	2	0	1	30.9	27	0	2	0	1	37.0
8	1	3	0	2	30.1	18	0	2	0	1	32.5	28	0	2	0	1	37.4
9	1	3	1	2	32.5	19	0	2	0	1	34.0	29	0	2	0	1	37.7
10	1	3	1	2	34.6	20	0	2	0	1	33.3	30	0	2	0	1	37.1

Studies have revealed that paintwork and pigment part of a composition can influence funginertness of coatings.

To a greater extent bottom layer influenced funginertness of coatings at 25% content of pigments: mineral bottom layer increased ability of coatings to inhibit growth of mold fungi. At 30 and 35% mas. filling of the film not only paintwork influenced funginertness but also pigment volume concentration. Among equally filled films compositions No. 16 and 17 consisted of maximal number of zinc oxide – pigment that inhibit growth of mold fungi (16.7 and 20 wt % correspondently) and had minimal value of pigment volume concentration (31.8 and 30,9% vol.). Composition No. 11 – minimal number of zinc oxide (10%) and maximal number of calcite (5%) –filling agent, stimulating growth of mold fungi, PVC value made 35.4% vol. – maximal among equally filled films. Compositions No. 16 and 17 on mineral surface showed 0 points, No. 11 – 1 point. At equal filling and equal funginertness of unsupported film, compositions with less pigment volume concentration had better bioprotective properties on mineral bottom layer. At less value of PVC, pigments did not build barrier-layer effect.

At 35% of pigment content all samples showed funginertness while testing according to methods 1 and 2. Composition No. 21 with maximal pigment volume concentration showed the best physical and mechanical properties together with its bioprotective properties.

Technical characteristics of bioprotective paintwork material are in Table 3. With the help of the provided conditions it became possible to establish processes taking place in the coating in case of aggressive environments exposure due to the work of mold fungi. Every two days samples of coatings were processed by organic acids solution air-spraying. The content of the solution was similar to products released by mold fungi [3]. In 14 days the samples were exposed to IR-spectrum analyses (Fig.4). It can be seen from the figure that zinc oxide being a part of the content of the coating suppresses the activity of acids forming zinc oxalate salt (peak 1603 cm^{-1}), thus, it prevents changes in the structure of a film forming agent that are possible under conditions acid catalysis.

Table 3

Technical characteristics of the developed paintwork material

Indicator name	Value
Non-volatile matter content, %, not less	50
pH paints	8.5–9.1
Drying time till the rate of 3 at temperature (20 ± 2)°C, h, not more	1
Degree of grinding, micron, not more	40
Coverage rate of dried film, g/m^2, not more	80
Adhesion, MPa, not less	2
Film resistance to water static effect at temperature (20 ± 2)°C, h, not less	48
Nominal light-resistance, h, not less	24
Vapor transmissivity, $mg \cdot m^{-2} \cdot h^{-1} \cdot Pa^{-1}$	0,008
Funginertness according to NSS 9.050, point method 1 / method 2	0 / 1

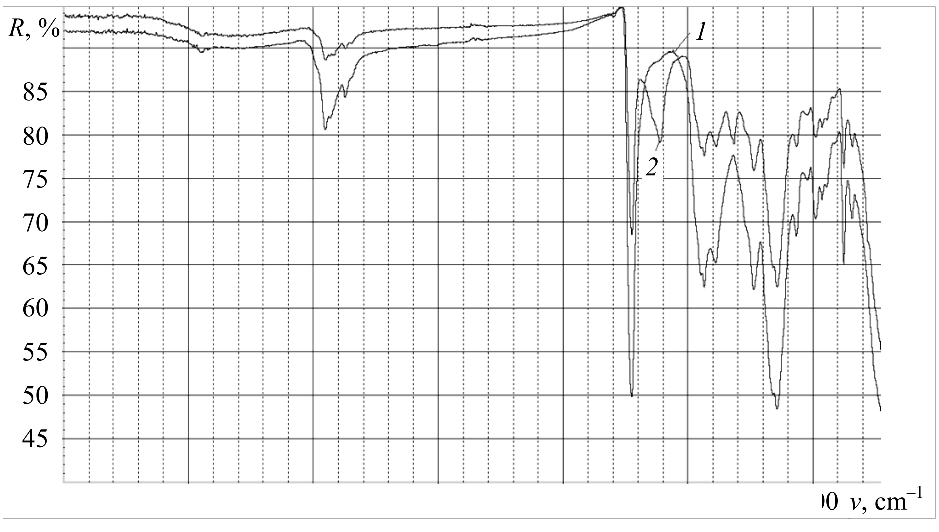

Fig. 4. IR- spectrum of bioprotective paint-and-laquaers coating until and after procession:
1 – initial coating without procession; *2* – coating after procession

Thus, paint coating is able to resist metabolites destroying action releasing by mold fungi.

Conclusion. The studies have shown the possibility of creation of highlyecological bioprotective paintwprk material on mineral bottom layer without biocidal additive. Composition No. 21 consisting of 15% of titanium dioxide, 15% of zinc oxide and 5% of calcite and maximal content of pigment volume concentration has shown the best bioprotective and working properties. It is shown that coating is able to resist destroying action of aggressive environments releasing by mold fungi.

Reference

1. Моргулец Е. Н., Прокопчук Н. Р., Гончарова И. А. Исследование влияния пигментов и водно-дисперсионных пленкообразователей на биостойкость лакокрасочных // Доклады НАН Беларуси. 2009. Т. 53, № 2. С. 65–68.

2. Сабадаха Е. Н., Прокопчук Н. Р., Гончарова И. А. Влияние метаболитов грибов на физико-механические свойства лакокрасочных покрытий // Труды БГТУ. 2010. № 4: Химия, технология орган. в-в и биотехнология. С. 306–309.

3. Выделение кислот некоторыми гифомицетами / А. А. Малама [и др.] // IV Всесоюзная конференция по биповреждениям: тезисы докладов, Н. Новгород, 3–6 октября 1991 г. / Нижегор. Гос. ун-т им. Н. И. Лобачевского, Науч.-исслед. ин-т химии; редкол.: В. Д. Ильичев [и др.]. Н. Новгород, 1991. – С. 51.

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