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Organomineral Additive for Dry Mixes

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Abstract: The data on technology of receiving organomineral additive on the basis of clays with the raised content of montmorillonite were provided. The questions of surface-active substances adsorption on the surface of clays were considered. It was shown that application of organomineral additive in a compounding tender mixes promotes resistance increase to the slipping of mortars from a vertical surface.

Key words: Organoclay, adsorption, surface-active substances, dispersancy, dry construction mixes

INTRODUCTION

One of the problems at the performing decorative finishing works is still slipping of mortars after their drawing on vertical surfaces. For the improvement of rheological and technological properties of finishing structures, thixotropic additives one of which are organomineralny additives (Ben) are entered into their compounding. The only domestic analog of foreign organoclays (Ben) is organobentonite. Organobentonite is applied in various industries, including production of organodiluted coating compositions, oil and gas production, foundry production, sewage treatment, metal working, etc. The technology of receiving organomineral additive consists in adsorption of surface-active substance on bentonite clay (organomodification) (Kuo *et al*., 2006; Sarier and Onder, 2010; Günister *et al*., 2006). The most widespread method of organomodification is occurrence of salt of chloride alkyl ammonium type in the interlayered space of clay.

At the same time, the volume of organobentonite production is insufficient because of limitation in stocks bentonite (montmorillonite) clays. Due to the aforesaid, the problem of organomineral additives development on the basis of local mixed clays with the prevalence of montmorillonite (Loganina and Petukhova, 2008; Loganina *et al*., 2014) is actual.

The purpose of this work is the development of structures and production technology of organomineral additive on the basis of clays with the prevalence of montmorillonite with its subsequent application in decorative limy dry construction mixes (Vejmelková *et al*., 2012; Ventola *et al*., 2011; Loganina *et al*., 2014; Vejmelkova *et al*., 2012)

MATERIALS AND METHODS

Technique of carrying out researches: The clays applied in the work are characterized by various content of montmorillonite (Russia). The researches of exchange capacity of mixed clays were carried out for the comparison with bentonites. The results of experiments were given in the Table 1-3.

Table 1: Indicators of clays dispersion

Clay field	Value of specific surface, $S_{уд}$, m^2kg	Average diameter of particles, micron
Vorobyevskoye	1264	1.86
Belinskoye	1245	1.89
Kameshkirskoye	1200	1.96
Lyagushovskoye	1288	1.83

Table 2: - Chemical composition of clays

Chemical compound	Content of chemical compounds depending on clay field (%)			
	Belinskoye	Kameshkirskoye	Vorobyevskoye	Lyagushovskoye
SiO_2	59.56	75.41	72.76	65.50
Al_2O_3	11.85	11.04	11.57	9.54
Fe_2O_3	4.54	6.61	7.39	7.72
Other	24.05	6.94	7.72	15.46

Table 3: Capacity of cationic absorption of the studied clays

Clay field	Value of cationic absorption capacity E, mg•eq
Vorobyevskoye	11.79
Belinskoye	20.48
Kameshkirskoye	42.50
Lyagushovskoye	39.73

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The analysis of clays on the capacity of cationic absorption allows claiming that clay of Vorobyevsky field belongs to kaolinite type of clays by mineralogical structure, Belinsky field to hydromicaceous type, Kameshkirsky and Lyagushovsky fields to montmorillonite.

Additives OP-4, OP-7, OP-10 and sulphanole were applied as an organic component at the developing of organomineral additive. The additive of OP-4 is a product at the developing of organomineral additive as an organic component additives nteraction of alkifenol with an ethylene oxide, surfactant belongs to the class nonionic. Additives of OP-7 and OP-10 are in a type of transparent liquid of yellow color. These substances are products of processing of mix mono and dialkilfenol an ethylene oxide, possessing alkalescent or subacidic reaction. Belong to the class nonionic surfactant. Sulfanol is a sodium salt of alkyl benzene sulfonic acid-powdery substance of white color.

Adbsortion of surfactants on clay surfaces, dispersancy of clay in water by the method of sedimentary analysis were determined for the receiving of organomineral additive. Clay was entered into the solution of additive for the determination of adsorption size of organic component on clay surface. Then the solution was mixed up and settled till the adsorptive balance.

The value of adsorbed substance was determined by the change of superficial tension of softener water solution σ_s owing to the decrease in concentration of adsorbate at the addition in clay solution. Definition of superficial tension was carried out by the method of drops account (stalagmometric method). On the change of superficial tension, optimum concentration of softener was established when σ_s = const.

The efficiency of organomineral additive application in finishing compounds was estimated on their resistance to slipping from a vertical surface. The assessment of slipping resistance of finishing layer consisted in the following. Finishing layer with thickness δ and height h is rigidly fastened to wall material (substrate). The layer is loaded with volume forces ρ. On the layer border, there is a tangent tensions τ which keep the considered layer in balance. For assessment of coat layer balance condition (lack of "slipping") it is possible to use inequation:

$$\left|\tau_{max}\right| = 4\gamma\delta \leq \tau_s \quad (1)$$

Where: γ is average density of finishing-coat material

$$\tau_s = \tau_0 + \tau_{ad} \quad (2)$$

Where:

τ_s = Summarized from the limit tension of shift

τ_0 = Rheological characteristic and adhesive durability of covering and substrate τ_{ad}

Considering that finishing layer size τ_{ad} is very small at the initial moment of drawing, the Eq. 2 can be written down as:

$$\tau_{max} < \kappa\tau_0 \quad (3)$$

Where, k-coefficient considering the contribution of adhesive durability to the condition 2. Equation 3 can be used for the determination of covering optimum thickness excluding its slipping from a vertical surface.

For the assessment of organomineral additive influence on slipping resistance of finishing solution, the following tests were carried out. The structures on the basis of dry construction mixes of 12 mm thickness were applied on the glass plate and surface from cement and sand solution located horizontally then plates were lifted in vertical situation. Plate tilt angle was defined at which slipping of finishing solution was observed. Structures with the application of additive organobentonite were prepared for the comparison in amount of 1% of lime mass. The control one was limysand structure with quartz sand with I:P ratio = 1:4. Water Limy ratio (W/L) thus was W/L = 1.4. The content of organomineral additive was from 1-10% of lime mass.

In the research, slipping resistance of finishing layer was additionally estimated by visual method according to EH 998-1. For this purpose, the plate with the applied solution is put in vertical situation (by plate length) and is kept within 30 min. The studied solution should not flow down.

RESULTS AND DISCUSSION

It was determined that value of superficial tension remains constant at the excess of sulphanole additives concentration >0.2%, OP-10 and OP-7 >0.5%, OP-4 >2% and is respectively $\sigma = 24.2$ Jm^{-2}, $\sigma = 28.8$ J m^{-2}, $\sigma = 29.1$ J m^{-2} и $\sigma = 27.0$ J m^{-2}.

It was determined that adsorption of additive OP-4 on vorobjevsky clay from 0.1 and 0.2% solution concentration comes in 10 h and 0.5 and 0.7% concentration in 48 h. Time necessary for full adsorption of sulphanole from 0.02 and 0.05% solution concentration are 10 h while from 0.07 and 0.1% concentration 22 h.

It was determined that full adsorption of OP-7 and OP-10 on the studied clays comes in 10 h at 0.02% concentration of solutions and in 48 h at 0.2 and 0.5% concentration. Results of experimental data testify that OP-10 additive in comparison with additive OP-7 possesses bigger adsorptive ability. So, values of adsorption at concentration of OP-7 and OP-10 solutions, equal to 0.5% were for vorobyevsky clay, respectively

Table 4: Constants of Langmuir equation characterizing adsorption surfactant on clays

	Value of adsorption at surfactants maximum concentration, α_∞. 10^{-4}, kg m^{-2}		Value of adsorptive balance constant, b, 1/%	
Clay field	OP-7	OP-10	OP-7	OP-10
Vorobyevskoye	2.183	2.308	0.3713	0.4266
Belinskoye	2.258	2.517	0.4080	0.4923
Lyagushovskoye	2.375	2.817	0.4352	0.6146
Kameshkirskoye	2.442	2.992	0.4603	0.6941

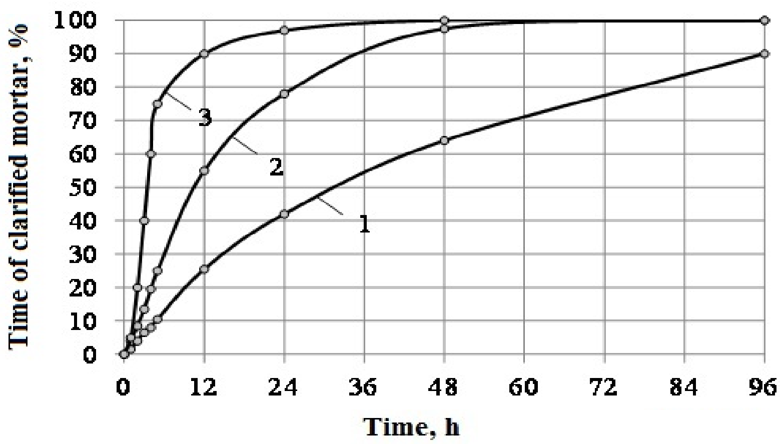

Fig. 1: Curve of particles sedimentation

A = 2.183×10^{-4} kg m^{-2} and A = 2.308×10^{4} kg m^{2} for belinsky clay A = 2.258×10^{-4} kg m^{-2} and A = 2.517×10^{-4} kg m^{-2} for kameshkirsky clay A = 2.442×10^{-4} kg m^{-2} and A = 2.992×10^{-4} kg m^{-2} for lyagushovsky clay A = 2.375×10^{-4} kg m^{-2} and A = 2.817×10^{-4} kg m^{-2}. Langmuir equation of isotherm adsorption was used for the description of static exchange:

$$a = \frac{a_\infty bC_p}{1+bC_p} \tag{4}$$

Where:

- α = Size of ions adsorption (kg m^{-2})
- α_∞ = Maximum adsorption corresponding to the full covering of mineral surface (kg m^{-2})
- b = Constant characterizing surfactants adsorbability
- C_p = Equilibrium concentration in solution (%)

Results of calculation and experiment were given in the Table 4. The received values of adsorbability b constants testify that additives OP-4 and sulphanole are the most inclined to the adsorption in comparison with other additives. The results of water dispersed ability assessment of the received organomineral additives in comparison with usual clay by the method of sediment analysis and influence of modified and control clay on particles subsidence in water solution were given in Fig. 1 and 2.

The results of researches (Fig. 1) showed that particles subsidence of clay modified by sulphanole, takes place more slowly than subsidence of control clay that is, particles of organomineral additive modified by sulphanole become more disperse in water solution.

Clay modified by OP-4 additive settles quicker than raw clay. Obviously, it is connected with oily consistence of the additive which gives oily texture to organoclay on the basis of OP-4. Organoclay on the basis of OP-4 does not peeled in water solutions and there is no more disperse in comparison with control clay. The received results testify to impossibility of additive OP-4 application as raw materials at the receiving organoclay for dry construction mixes.

Comparative researches of granulometric composition of clays of Kameshkirsky and for comparison, Vorobyevsky fields processed by additive OP-10 and in natural state were in addition carried out. The research of granulometric composition was conducted by pipette method. The results of experiments were given in Fig. 2.

It was established that modified clay is well dispersed in water: the content of small fractions increases and the content of large fractions decreases. So, the content of particles <0.001 mm in size in organoclay on the basis of Kameshkirsky field is 46%, fractions 0.01-0.005 mm 16% and in control structure 27 and 36% respectively.

The similar situation is observed in a case with vorobyevsky clay as well. The content of particles

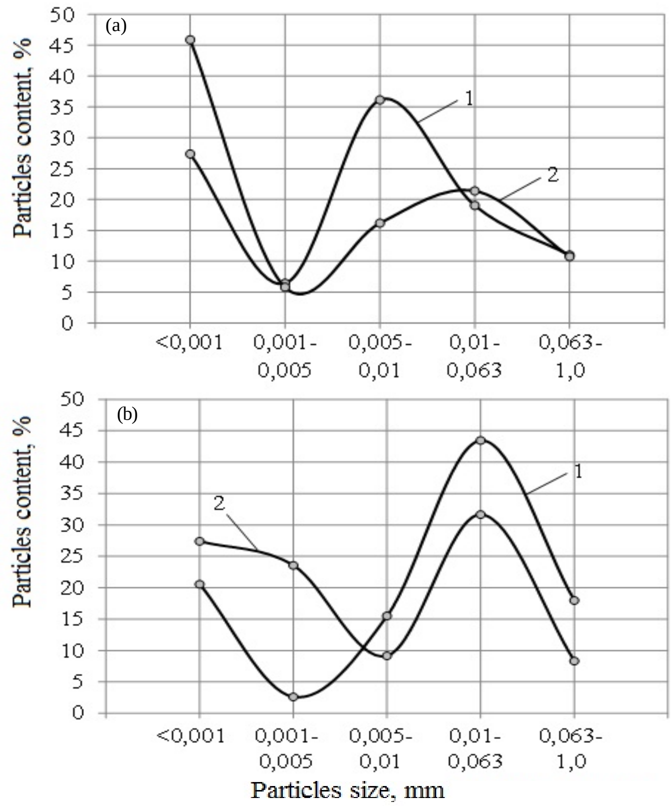

Fig. 2: Granulometric composition of clays of field; a) Vorobyevskoye: Not modified clay; clay modified by organic additive; b) Kameshkirskoye: Not modified clay; clay modified by organic additive

0.001-0.005 mm in size in organoclay is 23.5%, fractions 0.01-0.063 mm of 32% and in control structure 3 and 43.5%, respectively. Thus, modification of clays by organic additive promoted increase in the content of particles <0.001 mm in size in organoclay on the basis of Kameshkirsky field for 68%, on the basis of Vorobyevsky field for 33%.

The research results of adsorbing ability of clays testify that kameshkirsky clay possesses higher adsorbing properties in comparison with belinsky, vorobyevsky and lyagushovsky clays (Russia). Possibly, it is connected with mineral compositions of clays though all of them belong to mixed clays, nevertheless montmorillonite component in kameshkirsky clay has the prevalence (Fig. 2a, b).

Proceeding from the results of the carried out researches, it is recommended to use additives OP-7 and OP-10 and anion additive sulphanole at the receiving organomineral additive nonionic. Thus, depending on chosen surfactants, 38 g of additive OP-7 or 45 g of OP-10 or 46 g of sulphanole will be required for receiving 1 kg of organomineral additive.

The assessment results of application efficiency of organomineral additive in limy finishing mixes by the method of determination of finishing layer slipping resistance confirmed its efficiency (Table 5). Slipping resistance of finishing layer on the basis of studied structures at the thickness of 12 mm remains even at plate tilt angle, equal to 90° while slipping from the surface of glass plate happened already at 15° tilt angle. Therefore at the determination of limit tension of shift τ_s limy structures on glass substrate, the plate tilt angle was 14°. Such distinction is caused by the contribution of adhesive durability.

It was determined that introduction of organobentonite additives and organomineral additives on the basis of mixed clays leads to the decrease in plastic durability of finishing structure and increase of tangent tension values τ_{max} (Table 5).

The value of plastic durability τ_o and maximum tensions τ_{max} of control structure is $\tau_o = 8.48\times10^{-5}$ MPa and $\tau_{max} = 101.41\times10^{-5}$ MPa and at the introduction of organomineral additive in amount of 1%-$\tau_o = 4.58\times10^{-5}$ MPa and $\tau_{max} = 101.72\times10^{-5}$ MPa, respectively. Similar regularities are observed at the introduction of organobentonite as well.

The results of researches showed that adhesive durability of covering on solution substrate (Table 5)

Table 5: Influence of organomineral additives on slipping resistance of limy structures

Content (%)	Plastic strength, τ_o, MPa×10^{-5}	Maximum shearing stress, τ_{max}, MPa×10^{-5}	On mortar substrate: Coefficient k	On mortar substrate: Critical shear stress, $\tau_{cд}$, Mpa×10^{-5}	On glass substrate: Critical shear stress, $\tau_{cд}$, MPa×10^{-5}
Lime: sand = 1:4(control)	8.48	101.41	11.96	101.41	104.55
The same+organobentonite(1)	5.48	101.68	18.55	101.68	105.04
The same+organomineral additive(1)	4.58	101.72	22.21	101.72	105.08
The same+organomineral additive(3)	5.00	102.34	20.47	102.34	105.72
The same+organomineral additive(5)	5.34	102.95	19.28	102.95	106.35
The same+organomineral additive(10)	6.00	104.50	17.42	104.50	107.95

Table 6: Maximum values of tangent tension in finishing layer

Maximum values of tangent tension at layer thickness, τ_{max}, MPa×10^{-5}		
Values	1	2
10 mm	12 mm	15 mm
84.77	101.72	127.15

Table 7: Slipping resistance of finishing layer

Content(%)	Limit tension of shift τ_o, Mpa×10^{-5}	Layer thickness, mm: 5	10	12	15	17	20
И:П = 1:4. В/И = 1.4 (control)	8.48	-	+	+	+	+	+
И:П = 1:4. В/И = 1.4+organomineral additive (1)	4.58	-	-	-	+	+	+
И:П = 1:4. В/И = 1.4+organobentonite (1)	5.48	-	-	-	+	+	+
И:П = 1:4. В/И = 1.07+additive C-3 (1)	9.00	-	-	-	-	+	+
И:П = 1:4. В/И = 1.07+organomineral additive (1)+additive C-3 (1)	10.10	-	-	-	-	-	-
И:П = 1:4. В/И = 1.07+organobentonite (1%)+additive C-3 (1)	9.33	-	-	-	-	-	-
И:П = 1:4. В/И = 1.07+organomineral additive (1)+additive C-3 (1)+additive mowilith pulver DM 1142 P (1%)	12.34	-	-	-	-	-	-

Sign (-) means slipping lack, sign (+)-existence of finishing layer slipping

increases at the introduction of organomineral additive. At the same time, the greatest values of the coefficient considering contribution of adhesive durability to the condition (3) are observed in the structures with organomineral additive in amount of 1% of lime mass (k = 22.21). With the increase of organoclay content, maximum tangent tension τ_{max} increase at the reduction of adhesive durability $\tau_{aд}$.

Proceeding from the data of Table 5, it is possible to say that both maximum tension and forces of mortar mix adhesion on glass substrate increase with the increase of organomineral additive content as a part of mix due to which limy structure keeps slipping resistance to the plate tilt angle-15°. The values of tangent tension in a finishing layer at various thickness of its drawing were calculated on a vertical surface (Table 6).

It was determined that maximum values of tangent tension at the thickness of finishing layer of 10-15 mm is τ_{max} = 84.77×10^{-5}-127.15×10^{-5} MPa that is much higher than plastic durability. However slipping of finishing mortar happens only at the thickness of 15 mm. Obviously, slipping resistance of finishing layer previous to the thickness of 12 mm is caused by adhesive durability contribution τ_{ad}.

At the assessment of slipping resistance by visual method it was determined that control structure is characterized by low slipping resistance. The finishing layer on the basis of such structure possesses slipping resistance only to the thickness of 5 mm but structure from organomineral additive keeps slipping resistance to the thickness of 15 mm. The same results arrive at the introduction of organobentonite additive to the compounding as well.

Introduction of C-3 supersoftener to limy and sand structure allows increasing some slipping resistance to the thickness of finishing layer of 17 mm. The existence of C-3 additives and organoclay in the mortar mix compounding allows increasing slipping resistance to the thickness of finishing layer of 20 mm. Introduction of redispersible powder Mowilith Pulver DM 1142 P to the compounding of additive promotes increase of structure adherence to the trimmed surface, increase of plastic durability that in general promotes increase of structure slipping resistance. The similar regularity is observed in the structures with filler from lower-ablyazovskogo pit (Table 7).

The shift of rather rigidly fixed line of the top layers of the finishing layer applied with the thickness of 12 mm on a concrete surface was additionally estimated. Experimental data showed that shift of finishing layer on the basis of control solution was 1 mm, on the basis of structure with organoclay in amount of 1% of lime mass-0.3 mm and at the content of organoclay of 3% and above shifts was not observed. The shift is also absent at the introduction of organobentonite additive in amount of 1% to the compounding.

CONCLUSION

The technology and compounding of organomineral additive for dry construction mixes consisting in adsorption anion and nonionic surfactants on a surface of mixed clays with the raised content of montmorillonite was developed. It was offered to apply clay of Kameshkirsky field at the production of organomineral additive to use nonionic superficial active substance OP-10 as organic additive. The size of OP-10 additive adsorption is $0.375 \cdot 10^{-4}$ kg m^{-2}.

It was determined that introduction of limy dry mix of organomineral additives on the basis of mixed clays of Penza region to the compounding promotes increase of finishing layer slipping resistance. 20 mm optimum thickness of finishing layer at which slipping from a vertical surface is not observed was determined.

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