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PREPARATION OF FILLERS BASED ON HYDRATED ALUMINIUM ORTHOPHOSPHATE FOR ERS

In this paper, aluminum orthophosphates of the monoclinic and orthorhombic structure of $AlPO_4 \times 2H_2O$ (metavariscite and variscite, respectively) and modified H_3PO_4 of $Al_2O_3 \cdot nP_2O_5 \cdot xH_2O$, where $n = 1.1-1.2$, are obtained by the method of isothermal crystallization of aluminophosphate solutions. It is noted that the monoclinic modification is formed from concentrated solution (380 g $P_2O_5 \cdot l^{-1}$), orthorhombic – from a dilute (12 g $P_2O_5 \cdot l^{-1}$). According to the results of thermal and infrared spectroscopic studies it is developed that the energy state of the crystal water molecules in the variscite and metavariscite differs significantly. It is shown that the bond of the crystal water molecules for metavariscite is stronger than for variscite. Fillers for electrorheological suspensions on the basis of the synthesized aluminum orthophosphate are obtained by partial dehydration. The activity of fillers on the base of metavariscite ($\tau_E / \tau_{E=0} = 43-50$) is significantly higher than that the base on the variscite ($\tau_E / \tau_{E=0} = 8$). It is suggested that the concentration of charge carries depending on the degree of protonation of proton containing groups in a layered monoclinic structure of metavariscite and their mobility is higher than the concentration and mobility of the protons in the close-packed structure varistcite. It was shown that the presence of phosphoric acid at the surface of the solid phase has almost no effect on value of the electrorheological activity.

Key words: aluminum orthophosphate, variscite, metavariscite, structure, water, electrorheological suspension, electrorheological activity, current density.

Introduction. Aluminium phosphates due to the variety of their composition and properties are used as a ceramic binder in the production of anticorrosive materials, catalysts and in medicine. According to this article [1] acidic aluminium phosphates can have proton conductivity properties because of displaqcement of portable protons on the surface or volume of substance. Surface proton conductivity is a condition for electrorheologic activity of these compounds. In the papers [2, 3] electrorheologic activity of acid phosphates of zirconium, indium, tallium, aluminium as a dispersed phase of electrorheologic suspensions (ERS) have been studied, in which the main charge carriers are hydrobased protons, generated by dissociation of P-OH groups. Thus, according to [2], there is transferring of proton to the water molecule along the line of considerably strong hydrogen bond. Information about electrorheological activity of other hydrated phosphates of polyvalent metals is segmentary and limited. At the same time, taking into consideration a specific state of water molecules, connected with the influence of the electrostatic field of the cation and donor-acceptor properties of orthophosphate anion, not only acidic but also medium phosphates of metals, in particular, aluminium which crystallizes in the form of crystalline $AlPO_4 \times 2H_2O$ in two modifications (orthorhombic and monoclinic) depending on the conditions of ob-

taining are of interest for the research as a dispersed phase or ERS fillers.

The aim of this work is to obtain fillers for ERS on the basis of hydrated aluminium orthophosphates and studies dependencybetween their electrorheological activity and their composition and structure.

Methods of experiment. The process of obtaining of orthophosphates of alluminium consisted of following stages: preparation of alumophosphate solution, isothermal crystallization of aluminium orthophosphate, filtering and washing of the sediment and drying. Alumophosphate solution was prepared by dissolving of aluminium hydroxide, solution mark is "p" (pure), in the solution of thermal phosphoric acid containing H_3PO_4 equal to 50.0 wt %. Crystallization of aluminium orthophosphates has been carried out from the solutions in which mole ratio of P_2O_5/Al_2O_3 was 2.70, $H_2O/Al_2O_3 - 15.8$ and 503, while the content of P_2O_5 in the solutions was 380 and 12 g/l correspondingly. Prepared alumophosphate solutions were put into autoclave and kept during 12 hours at the temperature of $100°C$, resulting in the white colour sediment. The resulting suspension was cooled to the temperature of $55-60°C$ and filtered with the help of vacuum filter. Sediments were washed out with hot water at $90-92°C$ by decantation method. To obtain samples of orthophosphates of aluminium modifies by H_3PO_4, washing of the sediment has been carried out to the extent of washing less than 100%.

Table 1

Chemical and phase composition of the obtained aluminum orthophosphate

No. of sample	Degree of cleanning, %	The results of chemical analysis content by wt %			Gross composition	The values of interplanar distances d, Å	Structure, the mineralogical name
		Al_2O_3	P_2O_5	H_2O			
1	99.9	32.3	44.9	22.8	$Al_2O_3 \cdot P_2O_5 \cdot 4,0H_2O$	5.36, 4.260, 3.041, 2.914, 2.871, 2.633	Orthorhombic, variscite
2	99.9	32.3	44.9	22.8	$Al_2O_3 \cdot P_2O_5 \cdot 4.0H_2O$	6.325, 4.758, 4.552 3.503, 2.705, 2.290	Monoclinic, metavariscite
3	85.5	27.2	41.6	31.2	$Al_2O_3 \cdot 1.1P_2O_5 \cdot 6.5H_2O$		
4	76/0	25.1	42.0	32.8	$Al_2O_3 \cdot 1.2P_2O_5 \cdot 7.4H_2O$		

Note. The samples were dried at 50°C to constant weight.

The extent of sediment washing has been controlled on the content of P_2O_5 in the solid phase and washing waters which was calculated by the formula

$$CO = \left(1 - \frac{m'_{P_2O_5} - m''_{P_2O_5}}{m''_{P_2O_5}}\right) \cdot 100\%,$$

where m'_{P2O5}, m''_{P2O5} – the mass of P_2O_5 in the solid phase before and after washing, correspondingly, g.

Drying of sediments has been carried out in the drying cupboard in cups of Petri at the temperature of 50°C to constant weight. Fillers for electrorheological suspensions were obtained by partial dehydration of the dried orthophosphates of aluminium in the temperature range of 50−105°C. Thin layer powdered orthophosphates of aluminium were poured into a cups of Petri and kept at a predetermined temperature as long as the mass was becomes constant then sieved through a sieve with $d = 0.063$ mm.

The content of Al_2O_3 in the tested samples was determined by chelatometric method by means of back titration of 0.1 n trilon B excess with solution of $ZnCl_2$ in the presence of selenology orange indicator. To determine the content of P_2O_5 photocolorimetric method was used, the essence of which is to measure the optical density of the solution at a wavelength of 450 nm, the amount of water was determined by the gravimetric method. The phase composition of the synthesized compounds was specified by means of 08 Advance diffractometer of Bruker AXS company (Germany). Measurement of the shape and size of the particles was performed with scanning electron microscope Jeol JSM − 5610LV (Japan). Thermal analysis of the synthesized products was carried out with derivatograph Paulik-Paulik-Erdey Q-1500 (Switzerland) in polythermal mode and the moisture meter Sartorius (Germany) in isothermal conditions. Infrared spectra were recorded on IR-Fourier spectrometer NICOLET NEXUS company (USA).

ERS was prepared by grinding the filler in transformer oil (added dropwise) in agate mortar to a uniform consistency. The filler content in the suspension was 10.0 wt %. A pilot assessment of the sensitivity of electrorheological suspensions at room temperature was carried out on the rotary viscometer Rheotest 2.1 (Germany). The leakage current was measured by M1109 milliammeter with a scale division of 1 μa.

Main part. Feature image of the aluminum orthophosphate obtained from alumophosphate solutions with different concentration of P_2O_5, and different cleaning degree are shown in Table 1.

Sample No. 1 was prepared from the diluted alumophosphates solution with a concentration of P_2O_5, 12 g/l, the samples No. 2–4 − from concentrate (380 g P_2O_5/l). According to the results of chemical and x-ray phase analysis, the sample No. 1 is orthophosphate of aluminum with orthorhombic structure, the samples No. 2–4 − orthophosphate of aluminum with monoclinic structure, which, according to [4], have the mineralogical name of variscite and metavariscite, respectively. According to the author [5] the fact of the formation of aluminum orthophosphate with different structure depending on the concentration aluminoceramic solutions is explained that hydrated aluminum ion $[Al(H_2O)_6]^{3+}$ in solutions of phosphoric acid forms a series phosphorus-containing aluminum complexes, water molecules and protonated orthophosphate anions and bound molecules H_3PO_4 can be ligands. Dissociation degree decreases when concentration of H_3PO_4 increas and the accumulation of dimers and more complicated formations of the polymerization takes place. Consequently, the composition and structure of aluminoceramic complexes formed in concentrated and diluted solutions, will be significantly different, which causes the formation of crystalline structures in which the elements of the crystal lattice are different. According to the Table 1

chemical composition of the samples No. 1 and No. 2 corresponds to the aluminum orthophosphate composition $AlPO_4 \cdot 2H_2O$. Chemical composition of samples No. 3 and 4 differs from the composition of sample No. 2, in spite of the same phase composition. First of all, it happens due to the presence of free phosphoric acid, as the degree of washing of these samples from H_3PO_4 was 85.5 and 76.0%. As a result, excessive amounts of P_2O_5, as compared with the stoichiometric is at 0.1 and 0.2 mol P_2O_5 (Table 1). Thus, variscite, metavariscite and modified H_3PO_4 metavariscite were the original samples to obtain the fillers.

According to the results of electron microscopic analysis, dispersed composition of variscite (Fig. 1, *a*) represented by large agglomerates and smaller particles. The small particles have an elongated shape, in which the length exceeds the width. The particle size of the variscite ranges from 5 to 200 μm. Morphological picture for metavariscite is different (Fig. 1, *b*). The number of small particles is much less, on photomicrographs large non-isometric forms particles whose largest dimension is 100 μm can be traced.
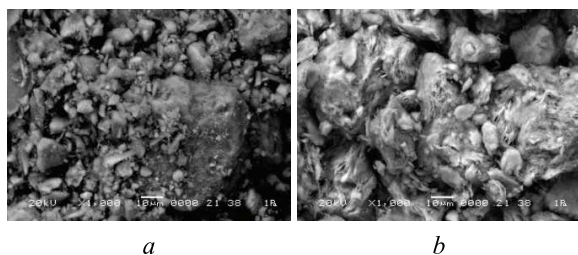

Fig. 1. Photomicrographs of samples No. 1 (*a*) and No. 2 (*b*) digidrata of orthophosphate aluminum (×1000 times)

According to the results of thermal studies of aluminum orthophosphate of monoclinic and orthorhombic structures in polythermal mode (Fig. 2), it was found that the mass of variscite begins to decrease at temperatures above 80°C and removal of all water takes place simultaneously in the area of the endothermic effect in the temperature range of 80–250°C with the minimum at 165°C.

The process of dehydration of metavariscite is characterized by two endothermic effects with minimums at a temperature of 115 and 180°C. According to the TG curve, mass loss of the sample at 115°C equals to 0.2 mol of H_2O and is not connected with the destruction of the crystal structure of metavariscite.

Release of the remaining quantity of hydrated water occurs in the temperature range of 140–300°C. According to differential drying curves, dehydration of variscite and metavariscite under isothermal conditions occurs in one phase, the transfer speed largely depends on temperature.
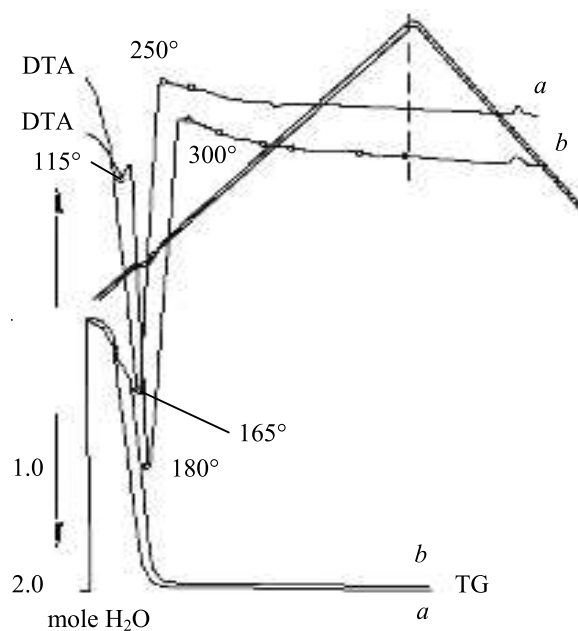

Fig. 2. Thermogram
of the sample No. 1 (*a*) and 2 (*b*)

At 80°C mass loss of variscite and metavariscite is practically not observed. Keeping of the present compounds at 95°C promotes processes of their dehydration. The variscite loses of 2.0 moles of H_2O (Fig. 3, *a*) and fully dehydrated, and metavariscite cleaves about 1.6 mol of H_2O (Fig. 3, *b*). At 100°C for metavariscite a complete dehydration takes place. It should be noted that the dehydration process of metavariscite at 100°C is more than 300 min, while complete dehydration of variscite at the same temperature occurs within 200 min, i. e. the speed of dehydration of variscite is significantly higher than metavariscite. Dehydration at temperatures of 110, 120, 130 and 140°C (Fig. 3, *a*, *b*) has the same pattern. At the temperature of 150°C there is almost complete dehydration of variscite and metavariscite within 80 min. Thus, according to the thermal analysis energy state of molecules of crystalline hydrated water in the variscite and metavariscite is a little different, at this metavariscite is characterized by stronger bond of H_2O molecules.

According to the data of thermal analysis on the basis of variscite and metavariscite fillers for ERS were tested, their temperature mode and chemical composition are presented in Table 2.

The criterion for evaluation of electrorheological activity of suspensions characterizing the degree of structuring of the dispersed phase particles in an electric field is the change in shear stress from the electric field. According to the results of the research activity of ERS containing the fillers of No. 2-1 and No. 2-2 as a dispersed phase, significantly higher than that of ERS-based filler No. 1-1 (Fig. 5).
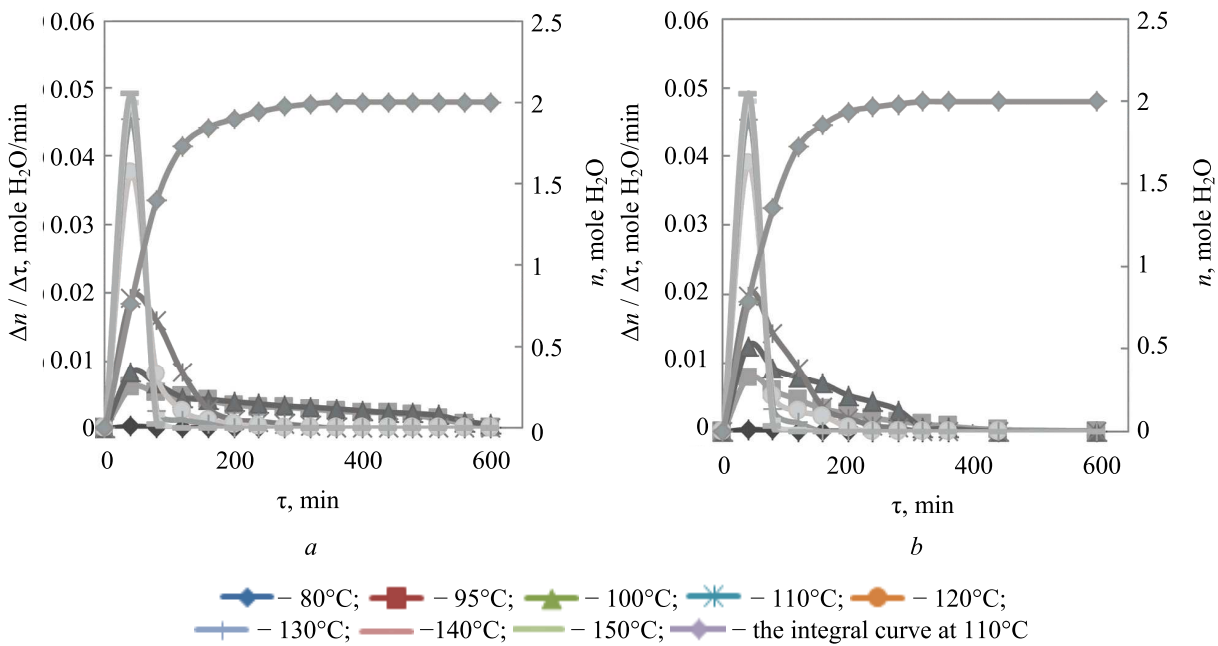
Fig. 3. Differential and integral curves of drying of the samples No. 1(*a*) and 2 (*b*)
under isothermal conditions

Table 2

**The conditions for obtaining fillers
for electrorheological suspensions and their composition**

No. sample	No. of filler	Temperature, °C	Duration, min	The gross composition of the filler
1	1-1	90	400	$Al_2O_3 \cdot P_2O_5 \cdot 1.2H_2O$
2	2-1	70	400	$Al_2O_3 \cdot 1.0P_2O_5 \cdot 4.0H_2O$
	2-2	90	600	$Al_2O_3 \cdot 1.0P_2O_5 \cdot 1.4H_2O$
3	3-1	70	400	$Al_2O_3 \cdot 1.1P_2O_5 \cdot 4.7H_2O$
	3-2	90	600	$Al_2O_3 \cdot 1.1P_2O_5 \cdot 1.3H_2O$
4	4-1	50	600	$Al_2O_3 \cdot 1.2P_2O_5 \cdot 4.3H_2O$
	4-2	85	600	$Al_2O_3 \cdot 1.2P_2O_5 \cdot 1.9H_2O$
	4-3	90	600	$Al_2O_3 \cdot 1.2P_2O_5 \cdot 1.2H_2O$
	4-4	105	240	$Al_2O_3 \cdot 1.2P_2O_5 \cdot 0.5H_2O$

Note. Sample number corresponds to the Table 1.

According to the data, the effective viscosity of a suspension based on metavariscite containing 4.0 mol of H_2O (filler No. 2-1) at the tension of 3.0 kV/mm, increases by 50 times, while for the filler No. 2-2 at the same tension is by 34 times. At further increase of the electric field (up to 3.5 kV/mm) in the case of filler No. 2-1, there is a "breakdown", and activity of filler No. 2-2 reaches 48. Such behavior of ERS based on fillers No. 2-1 and No. 2-2 under the influence of an electric field, primarily, stipulated by the amount of water and concentration of mobile protons resulting from dissociation of H_2O molecules depends on it. Under the influence of an electric field, the protons can move along the surface of the solid phase in the places with high tension, increasing proton conductivity. This explains high, restricting electrorheological activity, value of electric current density for the filler No. 2-1 (Fig. 4, *b*). The value of electrorheological activity for filler No. 1-1 on the basis of variscite at the strength of the electric field of $E = 3.5$ kV/mm is $\tau_E / \tau_{E = 0} = 8$, while for the filler No. 2-2 on the basis of metavariscite $\tau_E / \tau_{E = 0} = 47$, despite of almost the same amount of water (1.2 and 1.4 mol, respectively). A significant activity difference of ERS on the basis of the-

se fillers may be associated with different concentrations of charge carriers, which depends on the degree of protonized finish of protic groups and their mobility. According to this article [6] variscite is characterised by thick orthorhombic packing, as a result mobility of protons and speed of their migration on long distances in amount of the substance is likely to be smaller than in the structure of metavariscite.

It is known [7] that the degree of protonized finish is determined by the energy state of H_2O molecules, which, as it has already been noted, is significantly different in the structures of variscite and metavariscite, which is confirmed by IR spectroscopic studies (Fig. 5). According to the Figure, in spectra of variscite and metavariscite in the area of stretching vibrations of OH-groups, three bands are observed: two bands with frequencies at 3,380 and 3,100 cm^{-1} is characteristic for both compounds, the third at 3,590 cm^{-1} for variscite, at 3,460 cm^{-1} for metavariscite.

According to [8], a band with a maximum at 3,590 cm^{-1} corresponds to stretching vibrations of hydroxyl group. Shift of the bands of stretching vibrations of OH-groups of water molecules in the low frequency area indicates the presence of hydrogen bonds in the structure of these compounds. Analysis of bands of deformation vibrations of H_2O molecules in the IR spectra shows that, for

metavariscite, there is an intense band at 1,660 cm^{-1} due to the presence of H_2O, which maintained the molecular identity.

While a broad and diffuse band in the range of 1,500–1,700 cm^{-1}, is characteristic for the IR spectrum of variscite and can be determined by the special status of H_2O in the variscite. The authors of the article [9] assumed that one molecule of water in the composition of variscite is in dissociated and the other in molecular form, as a result, the composition of variscite is represented as an aqua complex of the type $[Al(OH)(H_2O)]HPO_4$. The structure of metavariscite can be characterized by the presence of groups $Al^{3+}...H_2O...OPO_3$, and the participation of two water molecules to form hydrogen bonds with oxygen orthophosphate anion. On the spectra of variscite and metavariscite splitting of the main absorption bands of the tetrahedron PO_4^{3-} is observed, which is manifested in the area of 1,200–900 and 650–400 cm^{-1}, which is a consequence of the strong distortion of orthophosphate groups. It should be noted that IR spectra of metavariscite modified with phosphoric acid (samples No. 3 and No. 4) entirely correspond to IR spectrum of sample No. 2.

Fig. 6 presents data of electro-rheological activity of fillers, obtained on the basis of metavariscite modified with different amounts of phosphoric acid.
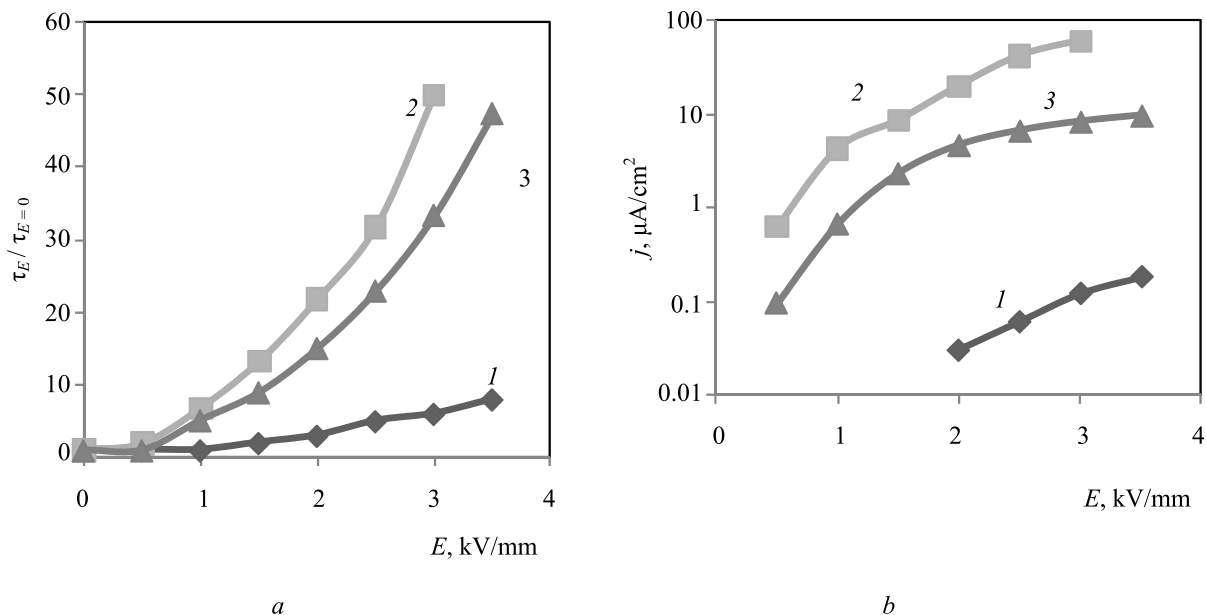

a   b

Fig. 4. Dependence of ER activity $\tau_E / \tau_{E=0}$ (a)
and current density j (b)
on the tension of suspensions electric field
based on digidrata of aluminum orthophosphate.
Shear rate $\gamma = 17.2$ s^{-1}, the concentration of filler = 10.0 wt %, $\tau_{E=0} = 2.8$ Pa:
1–3 − the suspension is based on filler No. 1-1, 2-1
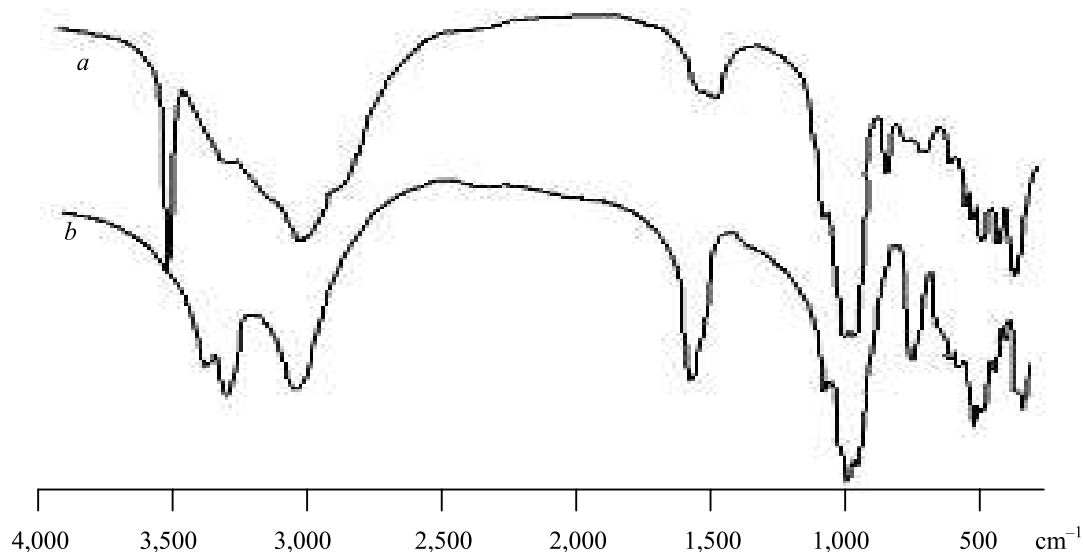and 2-2, respectively (numbering corresponds to the Table 2)

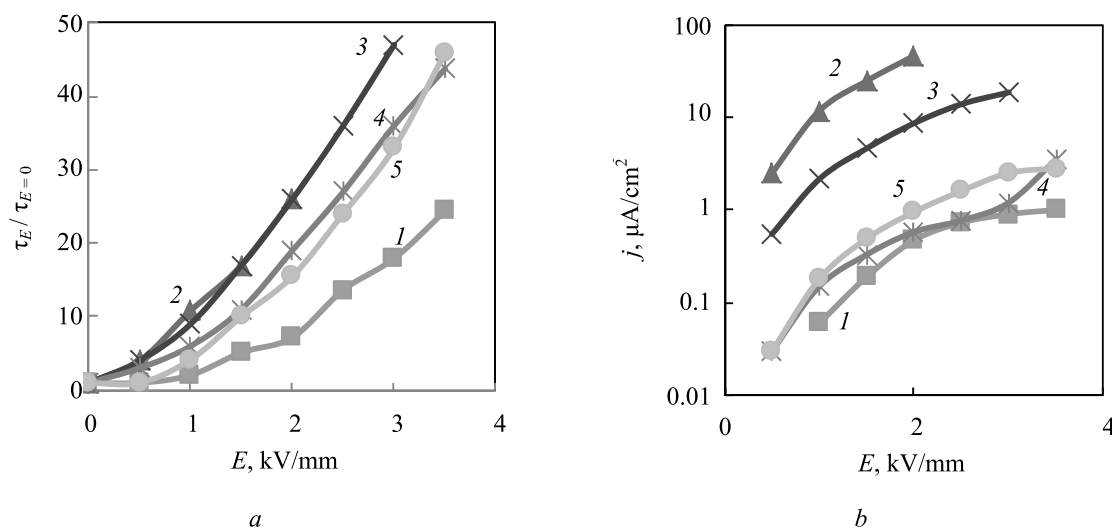Fig. 5. The IR spectra of samples No. 1 (*a*) and 2 (*b*)

a   *b*

Fig. 6. The dependence of ER activity $\tau_E / \tau_{E=0}$ (*a*) and current density j (*b*) on the tension of
the electric field of the suspensions based on metavariscite modified with phosphoric acid.
The shear rate $\gamma = 17.2$ s^{-1}, the concentration of filler = 10.0 wt %, $\tau_{E=0} = 2.8$ Pa:
1–5 − the suspension is based on filler No. 3-2, 4-1–4-4, respectively (numbering follows the Table 2)

According to the presented results, the electrorheological activity of these fillers (No. 3-2, No. 4-1–4-4) is on the same level (45–50) as the activity of the fillers of No. 2-1 and No. 2-2. It should be noted that fillers based on aluminum orthophosphate as stoichiometric and modified with phosphoric acid (fillers No. 2-1, 3-1 and 4-1), containing more than 4.0 mol of water, are characterized by "breakdown" because of the large limiting electrorheological activity values of the leakage current. For filler No. 4-2, containing 1.9 mole of water, the current density also has a high value (of 18.5 μA/cm^2) at an intensity of $E = 3.5$ kV/mm.

Electrorheological activity of fillers, containing from 1.4 to 0.5 mol of H$_2$O per 1 mol of Al$_2$O$_3$ (fillers No. 2-2, 3-2, 4-3, 4-4) is at the level of 43–50. The values of current density are in the range from 1 to 6 μA/cm^2.

Conclusion. Analysis and generalization of experimental data showed that the electrorheological activity of the fillers depends on the structure of the hydrated orthophosphate of aluminum, and the number of crystalline hydrate water remaining after partial dehydration of ERS on the basis of the monoclinic modification of aluminum orthophosphate having electrorheological activity at the level

of 45–50, on electrorheological activity they comparable with ERS based on the number of acidic phosphates of polyvalent metals. According to the complex experimental and literature data [3, 5, 7] we may suppose that molecules of water form protic groups that can dissociate under the influence of an electric field with the formation of the movable proton capable to move along the line of hydrogen bonds in a layered monoclinic structure of meta-variscite $AlPO_4 \cdot 2H_2O$.

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