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Characteristic features of the rheological behavior of dielectric layered-structure suspensions of hydrated metal oxides in an electric field

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Abstract. In this paper suspensions containing hydrated oxides of magnesium and iron were objects of rheological studies. The different content of the "stoichiometric" water in fillers is attributable to the conditions of their precipitation and aging. According to the results of TGA - DTA "super-stoichiometric" water of all the samples was removed in the temperature range 130 - 150°C, indicating its strong bond with the surface. Filler ER activity is determined by the change in the shear stress of the ER-suspensions containing them under the external electric field. The important role in the manifestation of the ER effect is played not only by the quantity of "super-stoichiometric" water in the interlayer space of the disperse phase particles, but also by the steric conditions.

1. Introduction

The uprising of the rheological indices of electrorheological fluids (ERF) under the action of an external electric field depends on the properties of a disperse phase whose role may be played by both water-containing and water-free compounds [1-7]. Some researchers [8-10] attribute the manifestation of the electrorheological (ER) effect to the presence of the adsorbed activator (the substance capable of forming hydrogen bonds such as hydroxyl-carboxyl-or amino-containing compounds) on the surface of the disperse phase particles. The most common activator is water entering into the composition of the water-containing disperse phase. The preparation of such disperse phase (ERF filler) is possible by means of both water adsorption in water-free compounds, more often oxide ones, and by chemical precipitation of hydrated compounds from aqueous solutions. In this case, the energy state of H_2O molecules and the form of their bonding in the hydrated filler may differ substantially and differently influence the ERF fluidity (viscosity, yield point, shear modulus, etc.). Water-containing ERF fillers, silicas (silica gel, aerosil, diatomite), metal oxides activated by H_2O adsorption have been studied most extensively. Occurring in this case is the filling of the surface of the particles with water and formation of polymolecular H_2O layers bound by the H bonds. The presence of film polarization ensures the transfer of charge carriers only along the particle surface. In an ERF based on particles with adsorbed water, the weakening or complete degeneration of the ER effect in time is possible especially on heating because of the irreversible desorption of weakly bound H_2O molecules.

In fillers based on hydrated compounds obtained by chemical precipitation, in addition to the structural and crystalline-hydrate H_2O there may also exists other O_mH_n groups capable of being preserved up to relatively high temperatures (200-250°C). They can potentially be used for creating thermally stable ERFs. The relationship between the nature, structure of O_mH_n groups in such type of fillers, and their rheological activity in an electric field is scarcely discussed in scientific publications. In the last 30 years, scientists of various countries have carried out numerous rheological investigations of ERF based on a water-containing disperse phase [1, 2, 4, 5 and 8]. In this connection, of particular interest is the investigation of the fillers of the ERFs, which are based on lamellar hydrated oxides of polyvalence metals, which, according to [11-13], consist of positively charged alternating two-dimensional metal-hydroxide layers, in the interlayer space of which the number of water molecules needed for ensuring the electrorheological (ER) activity of suspensions can be localized. The form and type of bonding as well as the quantity of H_2O molecules depend in the first place on the metal cation nature, structure of lamellar compounds, and on the conditions in which they were prepared. Moreover, in chemical compounds, the O_mH_n groups, which represent the interlayer water, can possess specific mobility, which exerts its influence on proton transfer and, correspondingly, on the magnitude of the conduction current.

Earlier [14, 15] we have studied the ER activity of the modifications of hydrated aluminum oxides (boehmite, pseudoboehmite, AlOOH, bayerity, Al(OH)₃), obtained by chemical precipitation under different conditions and differing in the type and quantity of H_2O molecules in them. It was shown [14] that fillers based on boehmite, $Al_2O_3 \cdot H_2O$, bayerite, $Al_2O_3 \cdot 3H_2O$, and containing only structural H_2O in the form of hydroxyl groups have a low ER activity. At the same time, the ERF based on pseudoboehmite which contains "super-stoichiometric" or unstructured water manifest a considerable ER effect. Such water molecules whose quantity is 0.25-0.8 mole per mole of Al_2O_3 are mainly localized in the interlayer space of the structure. It is shown that they are bound by strong hydrogen bridges in the boehmite lattice, are somewhat deformed, possess thermal stability, and are efficient activators of the disperse phase particles. The appearance of the proton conductivity in this case can be explained by the dissociation of H_2O molecules in an electric field with formation of protons and OH groups with strong hydrogen bonds. This ensures the appearance of strong structural bridges from disperse phase particles in an ERF.

Taking into account the role of the interlayer H_2O molecules in the initiation of the ER effect, as it is displayed in [14, 15], it is of scientific and practical interest to reveal the dependence of the ER effect on the quantity of active O_mH_n groups entering into the composition of lamellar hydrated compounds obtained by chemical precipitation. This will allow one to obtain new experimental data needed for elucidating the nature of proton-containing groups, their role in proton processes in a disperse phase for purposeful creation of electrically active and thermally stable fillers for ERFs.

The aim of the present work is investigation of the influence of the composition and structure of chemically precipitated hydrated magnesium and iron oxides on the ER activity of suspensions based on them.

2. Experimental

Electrosensitive particles of the filler of an ERF based on hydrated magnesium and iron oxides were obtained by the method of chemical precipitation in the metal salt-base-water system. As metal-containing reagents we used magnesium and iron chlorides. The precipitation of hydrate magnesium and iron oxides was effectuated in an alkaline medium, after which the sediment was kept for 6-8 hours under the liquid phase formed as a result of the chemical precipitation. Thereafter, it was separated from the liquid phase by filtering, washed and dried at a temperature of 20-30°C and then at 90°C up to a constant mass. The different content of the "stoichiometric" water in fillers is attributable to the conditions of their precipitation and aging. For the purposes of comparison we obtained hydrated aluminum oxide, the electrorheological properties of which were studied earlier in [14].

The compounds obtained were identified by the results of x-ray phase analysis with the use of a 08 Advance diffractometer of Bruker AXS Company (Germany). The content of magnesium and iron on

conversion into the mass of oxide, as well as the quantity of water were determined by the well-known methods. The dispersity of sediments was determined by a scanning electronic microscope "Jeol JSM-5610LV". The IR spectra of the compounds were obtained with the aid of a NEXUS IR-Fourier spectrometer of THERMO NICOLET Company. The thermal stability of the compounds was evaluated by the results of a differential-thermal analysis recorded by a thermoanalytical system TGA/DSC-1/1600 HF (METTLER TOLEDO Instruments, Switzerland).

The ER activity of the synthesized hydrated metal oxides was evaluated by the change in the shear stress of ERFs containing 10.0 wt.% of the filler in an dielectric oil under the action of electric field of strength from 0 to 3 kV/mm at the shear rate $\gamma = 17.24$ s^{-1}. The shear stress of ERF was measured by "Rheotest 2.1" rotational viscometer with an axially cylindrical cell at room temperature.

3. Results and discussion

The influence of the conditions of precipitation of hydrated metal oxides and their composition are presented in Table 1.

**Table 1.** Condition of precipitation of hydrated metal oxides and their composition

No. of sample	Nature and concentration of metal salt, moles/liter	pH of precipitation	Chemical composition	Phase composition
1	$MgCl_2$ 1.0	9.5-10.0	$MgO\cdot[H_2O]\cdot\{0.16H_2O\}$	
2	$MgCl_2$ 0.5	9.8-10.0	$MgO\cdot[H_2O]\cdot\{0.28H_2O\}$	$Mg(OH)_2$ (brucite)
3	$MgCl_2$ 0.05	9.9-10.0	$MgO\cdot[H_2O]\cdot\{0.45H_2O\}$	
4	$FeCl_3$ 0.5	12.0-12.5	$Fe_2O_3\cdot[H_2O]\cdot\{0.3H_2O\}$	α-FeOOH (goethite)
5	$Al_2(SO_4)_3$ 0.5	9.5-10.0	$Al_2O_3\cdot[H_2O]\cdot\{0.35H_2O\}$	AlOOH (pseudoboehmite)

[ ] –quantity of structured water

{ } – quantity of "superstoichiometric" water

According to the x-ray-phase analysis, the synthesized samples of fillers Nos.1-3 are crystalline hydrated magnesium oxides. They have a typical lamellar structure of brucite in which each Mg^{2+} ion is located between six OH groups and is bound with three OH ions of one layer and three OH ions of another one. Sample No. 4 is iron oxyhydroxide having the structure of goethite, which is a transitional one from a chain structure to a lamellar one. Its base is the densest hexagonal packing of O^{2-} ions, since the H^+ protons are located between pairs of O^{2-} ions not occupying particular space.

It has been established from the results of electronic-microscopic investigations that the synthesized samples of fillers are highly dispersed ones. Figure 1 presents microphotographs of samples No.2 and No.4, from which it is seen that they are polydisperse in composition. Sample No.2 (brucite) has particles of spherical shape of size 1-3 µm and their agglomerates of size 10-50 µm, pointing to the ability of primary particles to agglomerate. The prevailing size of the goethite particles (samples No.4) is 4.0-8.0 µm.
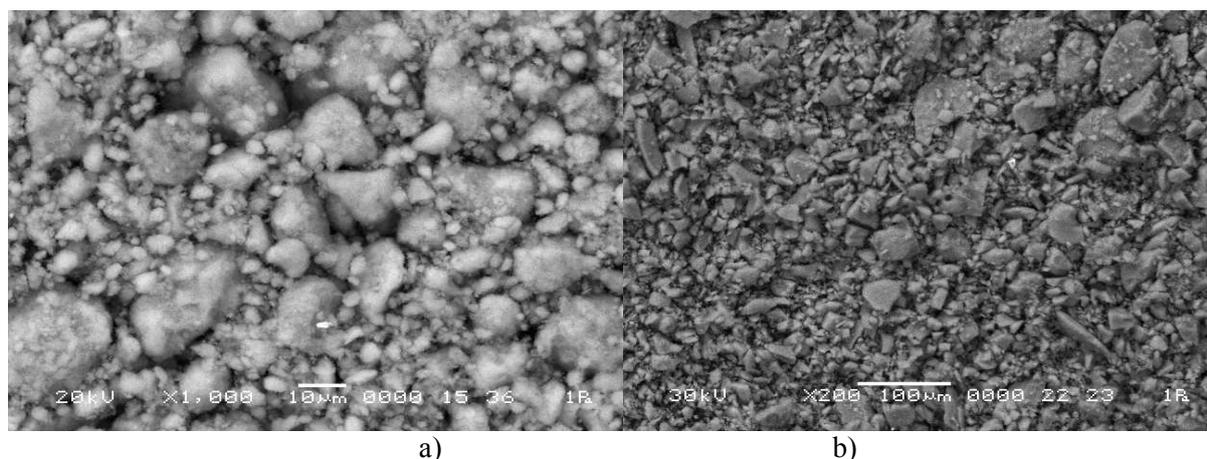
Figure 1. Microphotographs of a fillers sample No.2 (a), sample No.4 (b).

Proceeding from the stoichiometric composition of the indicated compounds, in particular, of $Mg(OH)_2(MgO \cdot H_2O)$, $FeOOH(Fe_2O_3 \cdot H_2O)$, in them, corresponding to 1 mole of metal oxide there is 1 mole of chemically bound or structural water, which in the form of OH groups participates in the construction of the crystal lattice. In addition to this type of water, the samples also contain "superstoichiometric" water. As shown in Table 1, its quantity for magnesium oxide depends on the precipitation conditions, in particular, on the concentration of the magnesium salt solution. Just as in the case of pseudoboehmite, the molecules of "superstoichiometric" H_2O can be both localized in the interlayer space of the lamellar structure of the compounds and adsorbed on the surface of crystals with which they are strongly bound by hydrogen bonds.

For the "superstoichiometric" H_2O molecules of brucite and goethite just as of pseudoboehmite, typical is the relatively high thermal stability, which is seen from the thermograms presented in Figure 2. The curves of heating the tested compounds have two endothermal peaks. The first, small peak is fixed in the region of T=100-250°C for brucite and T=100-230°C for goethite. The second, deep peak is located in the region of higher temperatures.
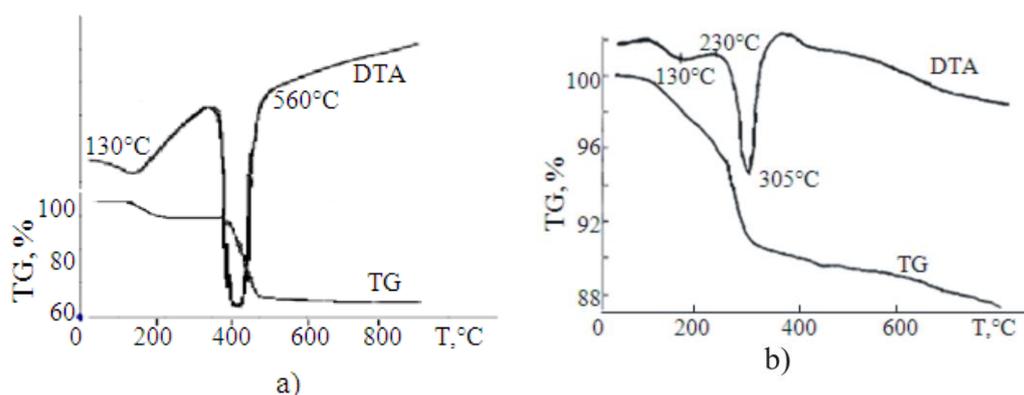
Figure 2. Thermograms of a fillers No.2 (a), No.4 (b).

Table 2 presents the results of the thermogravimetric analysis of samples No.2 and No.4 with indication of the amount of the removed H_2O in the region of the first and second endoeffects that was calculated from the thermogravimetric curves (TG) of samples shown in Figure 2.

Table 2. Results of thermogravimetric analysis

No. of sample	Amount of water removed, mole				
	Temperature interval, °C				
	90−130	130−200	200−360	360–560	560−800
2	0.23	0.05	0.0	1.0	0.0
4	0.10	0.19	0.74	0.09	0.19

As is seen from Figure 2, for sample No.2 the splitting out of 1 mole of chemically bound H_2O in the form of OH groups is fixed in the region of the second endoeffect at temperatures 360-560°C. In sample No.4, the chemically bound water is removed both in the region of the second endoeffect and on subsequent increase in the temperature, up to 800°C. In the temperature range 90-200°C, 0.28 and 0.29 moles of H_2O are removed from samples No.2 and No.4, respectively, which agrees with the amount of "superstoichiometric" water determined by gravimetrical analysis. Consequently, the "superstoichiometric" H_2O is removed from the region of the first endoeffect from both brucite and goethite. A comparatively high temperature of the dehydration of the "superstoichiometric" water molecules indicated the existence of strong H bond in them.

The energy state of H_2O molecules in brucite and goethite was estimated by the IR spectra in comparison with the results obtained for pseudoboehmite. The vibrational spectra of the compounds studied contain all basic features of the spectral display of hydrogen bonds in the O_mH_n groups (Figure 3).

The presence of the absorption bands (Figure 3) in the range 3700-3000 cm^{-1} indicates the formation of hydrogen bonds of different strength by H_2O molecules with the OH groups that were coordinated by the metal cation. For brucite, there is a narrow intense absorption band at 3700 cm^{-1} and a wide low-intensity band at 3436 cm^{-1}, as well as the absence of the bands of deformation vibrations of H_2O molecules in the spectrum. This may point to a specific energy state of the "superstoichiometric" H_2O in brucite initiated by the strong electrostatic field of the magnesium cation. Under its effect the OH bonds in water molecules can become weaker. Proceeding from the position of the band of valence vibrations of the OH groups of H_2O molecules an assumption can be made on the formation of strong hydrogen bonds in goethite, just as in the case of pseudoboehmite AlOOH.
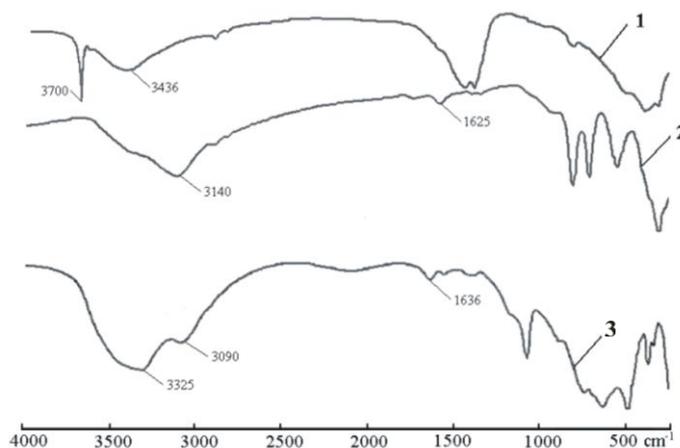

Figure 3. IR spectra of hydrated oxides magnesium, $Mg(OH)_2 \cdot 0.28H_2O$ (1); iron, $FeOOH \cdot 0.3H_2O$ (2); aluminum, $AlOOH \cdot 0.35H_2O$ (3).

The goethite, FeOOH, and pseudoboehmite, AlOOH, have the most similar IR spectra in the region of valence and deformation vibrations. However, the displacement of the bands of valence vibrations of the OOH groups of water molecules to the side of smaller frequencies is most typical of the IR spectra

of pseudoboehmite. This may mean that due to its small radius the Al^{3+} cation (0.51Å) is capable of very closely approaching the unshared pair of water molecules and attract them by its strong electrostatic field.

It was shown earlier [14, 15] that the energy state of H_2O molecules determined by steric conditions, polarizing action of the cation field, and by other factors is closely connected with the manifestation of the ER effect.

The dependences of the shear stress (τ) and current density (j) of ERF based on the studied hydrated magnesium, iron, and aluminum oxides on the electric field strength (E) are presented in Figures 4 and 5.
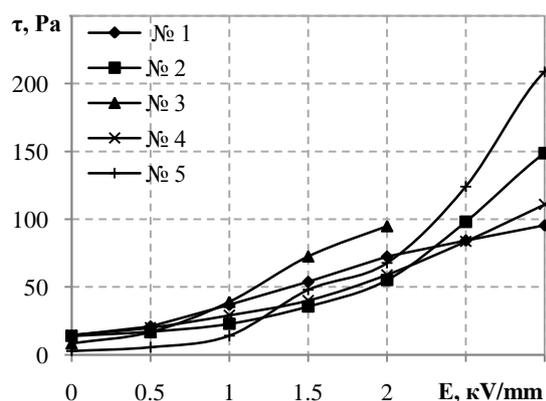
Figure 4. Dependence of shear stress on electric field strength for samples Nos. 1-5.
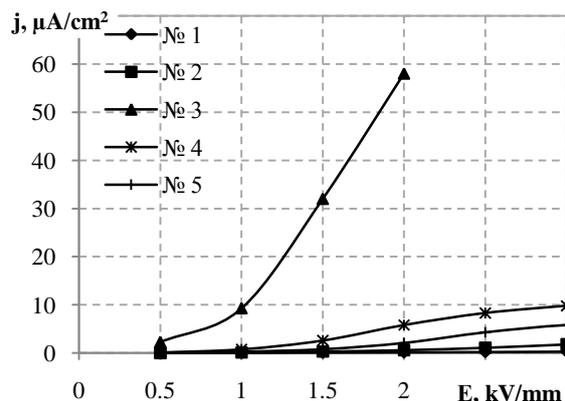
Figure 5. Dependence of current density on electric field strength for samples Nos. 1-5.

It should be noted that for the ERF based on brucite, which contains 0.45 moles of "superstoichiometric" water (sample No.3) a high current density (> 50 $\mu A/cm^2$ at E=1.5 kV/mm) is fixed. A further increase in the electric field strength leads to the overestimation of the threshold values of current density and to the break-down occurrence. On reduction of the amount of water in brucite to 0.28 moles (sample No.2) the current density also decreases, which allows one to increase the electric field strength up to 3.0 kV/mm and to attain the values of up to about 150 Pa for the shear stress of the ERF. A decrease in the number of moles of H_2O in brucite to 0.16 moles decreases the shear stress to 100 Pa (sample No.1). Thus, the intensity of the rise of the $\tau(E)$ curves for the ERF based on brusite is determined by the quantity of the "superstoichiometric" water. This seems to be associated with the concentration of mobile protons which depends on both the place of localization of water molecules and their energy state as well as on the steric conditions determined by the filler structure. It is seen form Figure 4 that at the content of the number of moles of "superstoichiometric" unstructured water close to about 0.3 moles in samples of brucite, goethite, pseudoboehmite (samples No.2,4,5, respectively) their ER activity does not differ substantially in an electric field of strength of up to 2.0 kV/mm. An increase in the electric field strength up to 3.0 kV/mm leads to a sharper increase in the shear stress of the ERF based on brucite, $Mg(OH)_2 \cdot 0.28H_2O$ (sample No.2) and pseudoboehmite, $AlOOH \cdot 0.35H_2O$ (sample No.5), which is less typical of the ERF based on goethite, $FeOOH \cdot 0.3H_2O$ (sample No.4). The strong shift of the band of valence vibrations of the OH groups of water molecules to the low-frequency region on the IR spectrum of goethite (3140 cm^{-1}, Figure 2) and their thermal stability make it possible to assume the presence of strong hydrogen bonds of H_2O molecules and the possibility of their protolytic dissociation in an electric field. It seems that by virtue of the specific features of the crystal structure of goethite, in which there are twinned layers of the densest packing of O^{2-} ions, the transfer of the proton over a great distance to oxygen atoms can be hampered. As a result, a continuous chain of hydroxyl groups that interacts via the hydrogen bonding and ensures the transfer of the charge by the proton mechanism is not formed. In the structure of brucite, the Mg^{2+} cations occupy all octahedron voids between two layers of OH groups located

according to the principle of the densest hexagonal packing, which ensures additional paths for the charge transfer in the interlayer space. In this case, for the transfer of the proton by the relay-race mechanism a small amount of H_2O is required, which is localized in the interlayer space. The increase in the shear stress in the ERF based on pseudoboehmite is larger than in the ERFs based on brucite and goethite, which contain 0.28-0.35 moles of "superstoichiometric" water at an electric field strength higher than 2 kV/mm. This is explained by the fact that, according to the IR spectra, stronger polarization is typical of the "superstoichiometric" water molecules in pseudoboehmite. It is determined by the donor-acceptor properties of aluminum and by the characteristic features of the structure of boehmite, in which the charge transfer may take place via the continuous network of the H bonds in the bulk of a substance, which plays the decisive role in the manifestation of the ER effect.

4. Conclusions

Thus, as follows from experimental data, despite the lamellar structure of all the ERF fillers studied, in the interlayer space of which approximately the same quantity of H_2O molecules is localized that form strong H bonds the ER activity of ERF differs substantially. This fact makes it possible to assume that the important role in the manifestation of the ER effect is played not only by the quantity of "superstoichiometric" water in the interlayer space of the disperse phase particles, but also by the steric conditions, i.e., by the characteristic features of the lamellar structure of fillers.

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