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INFLUENCE OF TEMPERATURE ON THE ELECTRORHEOLOGICAL RESPONSE OF DIELECTRIC SUSPENSIONS BASED ON A WATER-CONTAINING FILLER

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A study is made of the influence of temperature on the rheological properties of electrorheological fluids containing hydrated alumina in the form of pseudoboemite. It is shown experimentally that such electrorheological fluids possess thermal stability, preserving high indices of electrorheological activity (ER activity) up to 120°C. The use of pseudoboemite as a filler of electrorheological fluids will make it possible to ensure efficient operation of electrically controlled hydraulic devices with an extended temperature range of application.

Keywords: *electrorheological fluid, temperature, rheological properties, hydrated alumina.*

Introduction. Creation of electrorheological fluids that are efficient at elevated temperatures and can be used as dielectric heat-transfer agents with controlled characteristics for spherical heat exchangers in the operating temperature interval 70–150°C is a high-priority task.

It is common knowledge [1] that temperature exerts a strong influence on the manifestation of the electrorheological effect. It has been shown earlier [2–6] that electrorheological fluids based on both an inorganic water-containing dispersed phase and a water-free polymer dispersed phase show a higher electrorheological effect in heating. In the case of the water-containing filler this was attributed to the higher degree of polarization of the electric double layers and to the change in the viscosity of the dispersion medium. When water-free polymer particles of the dispersed phase were used, the enhancement of the electrorheological effect was related to the increase in the mobility, conductivity, and charge of the particles themselves with temperature.

Water-free electrorheological fluids compared to water-containing ones operate in a wider temperature range; however, we observe an undesirable increase in the conduction currents. Furthermore, the process of production of such suspensions is time-consuming and expensive. We know of the works [7] on creation of a water-free thermostable electrorheological fluid based on titaniumoxide particles that are coated with rare-earth metals, e.g., cerium. The electrorheological fluid based on such a complex filler shows the effect up to 110°C; the dependence of the shear stress on the temperature has a pronounced maximum at 80°C for all the investigated electric-field strengths, whereas the electrorheological fluid based on pure titanium oxide degrades even at 40°C.

The influence of the temperature on the rheology of electrorheological fluids based on lanthanum-containing carbon fibers in a polymethylsiloxane fluid has been investigated in [8, 9]. The lanthanum-containing carbon fibers were produced by impregnation of cellulose phosphate by the lanthanumchloride solution. Thereafter the fibers were dried and thermooxidized in air in the temperature interval 300–800°C for 0.5 to 3 h. Electrorheological fluids based on such a fibrous filler withstand heating to 130°C. The curves of effective viscosity as a function of temperature have a pronounced maximum at 100°C, on passage through which the effect begins to diminish.

Opinion exists [1] that most water-containing electrorheological fluids are capable of showing the electrorheological effect in a rather narrow temperature range, 20 to 70°C, and hence are unsuitable for heat exchangers and dynamic devices (dampers, couplings) heated as a result of energy dissipation in their operation. Thus, data on an electrorheological fluid based on water-containing cellulose (produced by the FMC Corporation) are given in [10]. Cellulose of two kinds with different amounts of adsorbed water (23.4% in TC40 and 20.6% in PH101) is used. Lubricating oil MVI100N produced by the Shell Oil Company serves as the dispersion medium. Shengbin et al. note that the electrorheological effect disappears even at 30°C in this system. Qualitatively analogous results have also been

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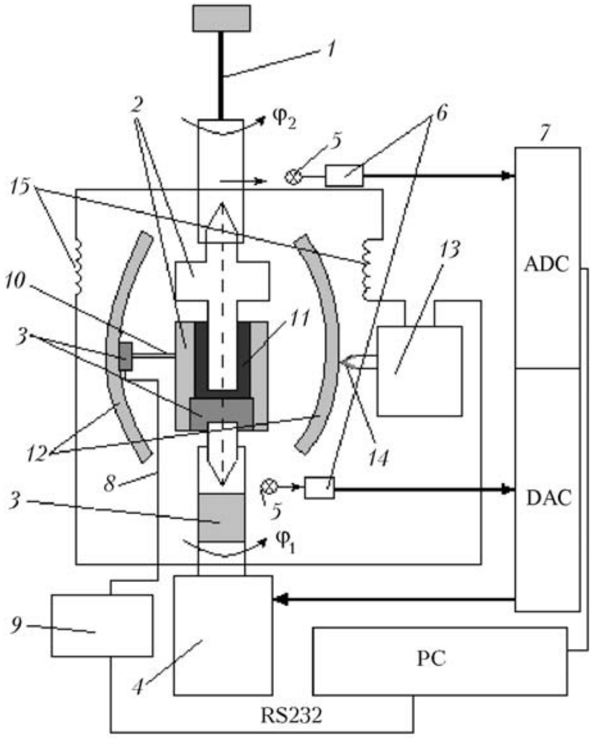

Fig. 1. Diagram of the measuring device: 1) torsion bar; 2) measuring unit; 3) insulators; 4) VR-74 drive; 5) sensors of the rotation angle; 6) filters; 7) PSL 812 personal computer (PC, computer, ADC, analog-to-digital converter, DAC, digital-to-analog converter); 8) current collector; 9) high-voltage source; 10) spring; 11) suspension; 12) emitting surface; 13) temperature regulator; 14) thermocouples; 15) heater.

obtained in investigating electrorheological fluids based on silica, diatomite, and alumina that were saturated with water by their soaking or holding in a steam atmosphere [11–13]. In heating above 60–70°C, the electrorheological fluid in such compositions virtually completely degenerates because of the irreversible desorption of water from the particle surface or its binding in combination with admixtures. High values of the current strength are recorded. In certain cases the current grows in an avalanche-type manner, up to the breakdown.

Inexpensive hydrated alumina in the form of pseudoboemite is of particular interest among water-containing fillers, since it makes it possible to attain a high electrorheological response of the electrorheological fluid based on it [14, 15]. We have made an assumption [14, 15] on the physical nature of electrorheological fluids in such dispersions, which starts from the fact that water molecules are linked by strong hydrogen bridges in the interlayer space of the alumina lattice and possess thermal stability. The present work seeks to establish the distinctive features of the influence of the temperature on the rheological properties of electrorheological fluids containing hydrated aluminum.

Experimental Procedure. The limiting shear stress τ_0 which is taken as the criterion characterizing the value of the electrorheological effect for highly filled electrorheological fluids, is measured with a VR-74 vibrometer (Fig. 1). The working unit of the device represents a cylinder–cylinder measuring system placed in a thermostat for keeping temperature constant. Electric potential is applied to the external cylinder; the internal cylinder is grounded. A constant rotational velocity is assigned to the external cylinder with the resulting development of flow with a constant deformation rate. Shear stresses arising in the material create a torque which is determined by measuring the rotation angle of a torsion bar connected to the internal cylinder.

The shear stresses are measured in a continuous-deformation regime for a constant rate of change in the deformation of 0.1 rad/min; the range of rotation angles is $\varphi = 0$–0.06 rad, which corresponds to the range of variation in the relative deformation $\varepsilon = 0$–200% and to a temperature of 18 to 120°C. The gap in the cell is 1.0 mm. The applied electric voltage is 0–2500 V.

TABLE 1. Characteristics of the Fillers of Electrorheological Fluids

Number of the sample of electrorheological fluid	Amount of water in the composition of the filler		Type of filler structure
	molar ratio Al_2O_3:H_2O	wt. %	
1	1:2.78	33.0	Weakly crystallized pseudoboemite
2	1:2.20	27.95	Pseudoboemite
3	1:2.01	26.1	>>

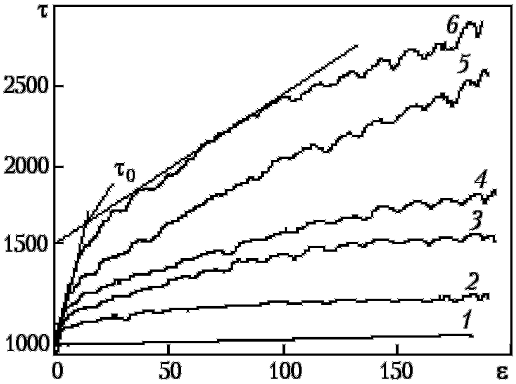

Fig. 2. Shear stress vs. applied deformation for sample No. 2 at 60°C for different electric-field strengths: 1) E = 0, 2) 500, 3) 1000, 4) 1500; 5) 2000, and 6) 2500 V/mm. τ, Pa; ε, %.

For certain values of the deformation and an assigned value of the electric-field strength, plastic flow develops in this unit. Therefore, the value of the shear stress for which elastic deformations become plastic ones is taken as the limiting value.

Hydrated alumina is produced by the method of chemical deposition with the subsequent stages of aging of the deposit, its washing off, drying, thermal treatment, and screening through a sieve with a mesh size of 0.05 mm [16]. The content of H_2O in the composition of the samples is determined thermogravimetrically with a derivatograph, whereas the content of Al_2O_3 is determined chelatometrically by the standard titration methods. The phase composition is established roentgenographically on a 08 Advance diffractometer of the Bruker AXS Company.

The produced aluminas with an assigned H_2O content are used for preparation of suspensions containing 40 wt. % of the indicated filler and 60% of transformer oil.

Table 1 gives the characteristics of hydrated aluminas used for preparation of electrorheological fluids. The samples under study represent weakly or well crystallized pseudoboemite with a variable water content.

It is common knowledge [17] that hydrated alumina in the form of pseudoboemite represents a highly dispersed disordered form of boemite γ-AlOOH ($Al_2O_3 \cdot H_2O$). Pseudoboemite consists of layered crystals of dimensions <100 Å, which are combined into larger porous aggregates. The layers are formed by double polymer molecules, and the interaction of the layers is ensured by hydrogen bonds. The superstoichiometric water in pseudoboemite is localized between the AlOOH crystalline layers and is linked by strong hydrogen bonds in the interlayer space of the boemite lattice.

The number of H_2O moles located in the interlayer space of pseudoboemite is known to be dependent on the conditions of its production, in particular, the conditions of deposition and thermal treatment. The weakly crystallized pseudoboemite (sample No. 1) contains 2.78 moles of H_2O of which 1 mole of H_2O is accounted for by the stoichiometric chemically bound water and 1.78 moles are accounted for by the interlayer and, in all likelihood, physicochemical water. The subsequent samples of the filler are characterized by the lower content of the physicomechanical water depending on the thermal-treatment temperature (see Table 1). The samples have a polydisperse composition with the dominant number of particles of diameter 1.65–1.7 μm.

Figure 2 plots the shear stress as a function of the applied deformation for sample No. 2. The obtained curves can arbitrarily be subdivided into two portions: the first portion describes elastic deformation, and the second characterizes plastic deformation and flow. The quantity τ_0 is determined from the point of intersection of the tangents to the lower and upper portions of the curves.

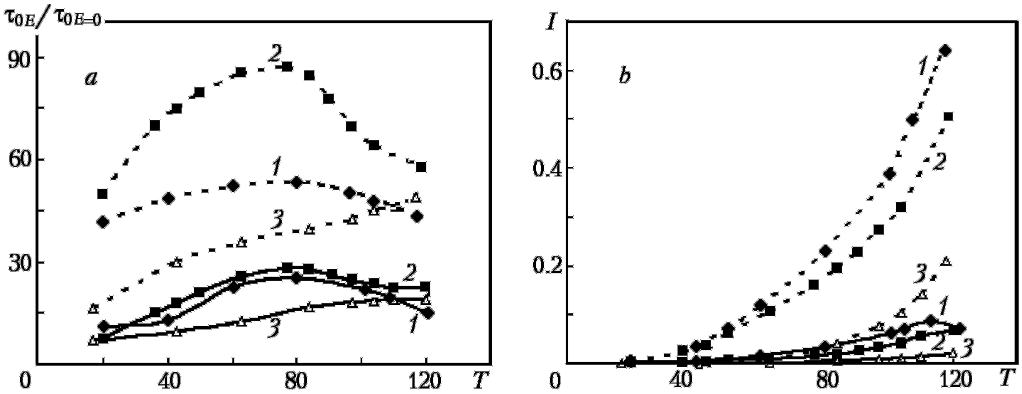

Fig. 3. Quantities $\tau_{0E}/\tau_{0E=0}$ (a) and I (b) vs. temperature: 1) sample No. 1 (33.0%); 2) No. 2 (27.95%); 3) No. 3 (26.1%); solid curves, E = 1000 V/mm; dashed curves, 2500 V/mm. I, mA; T, °C.

Experimental. Figure 3 plots the relative limiting shear stress (ER activity) and the cell current as functions of the temperature for electrorheological fluids based on hydrated aluminas for two electric-field strengths: 1000 and 2500 V/mm. The appearance of the $\tau_{0E}/\tau_{0E=0}$ (T) plots of the investigated samples differs: for samples No. 1 and No. 2 (see Table 1), they are extremum in character for all the investigated electric-field strengths, whereas for sample No. 3, they are of a nearly linear form (Fig. 3a). The highest $\tau_{0E}/\tau_{0E=0}$ values are shown by sample No. 2; for it, we observe a growth in $\tau_{0E}/\tau_{0E=0}$ up to 80°C; thereafter the values $\tau_{0E}/\tau_{0E=0}$ decrease, but at the maximum temperature (120°C) they still remain higher than at room temperature. For sample No. 3, $\tau_{0E}/\tau_{0E=0}$ monotonically grows with temperature throughout the investigated temperature range. It is not improbable that the extremum of the $\tau_{0E}/\tau_{0E=0}$ values for this sample is in the region of higher temperatures, which can be shown further with the use of a high-temperature dispersion medium.

A comparison of $\tau_{0E}/\tau_{0E=0}$ and I as functions of T (Fig. 3) shows that the largest ER activity is displayed by sample No. 2 having moderate current strengths I (curve 2). Sample No. 1, distinguished by the highest values of I (curve 1), displays ER activity weaker than sample No. 2. Sample No. 3 has the lowest values of both the conduction current and the ER activity (curve 3).

Figure 4 gives the comparative τ_0 (E) plots for electrorheological fluids based in diatomite (natural SiO_2 with admixtures of other inorganic oxides) and pseudoboemite. At room temperature, $\Delta\tau_0$ for the diatomite-based electrorheological fluid is 1.5 times higher than that for the pseudoboemite-based fluid. A monotonic increase in τ_0 (E) occurs to 40°C. In heating to 60–80°C, we find a maximum at E = 1500 V/mm and a further sharp decrease in τ_0 (Fig. 4a, curves 3 and 4). High values of the conduction current of the order of 1–1.2 mA are observed. The effect nearly totally degenerates in heating to 100°C (Fig. 4a, curve 5). The values of the conduction current are close to breakdown ones (>5 mA). Also, Fig. 4a shows that heating of the diatomite-based electrorheological fluid at 100°C produces irreversible changes, i.e., a reduction in its efficiency (curve 7) at room temperature (within 2 h after the heating). The values of the conduction current remain virtually constant (within 0.012–0.016 mA). For the pseudoboemite-based electrorheological fluid, the τ_0 values grow with field strength reqardless of temperature (Fig. 4b). The values of the conduction current in this sample are low (0.2 mA at 100°C). Heating of the pseudoboemite-based electrorheological fluid does not cause the electrorheological effect to diminish at room temperature.

Discussion of Results. An analysis of experimental data has shown that electrorheological formulas in which the dispersed phase is hydrated alumina in the form of pseudoboemite are characterized by the high electrorheological effect throughout the investigated temperature interval (20–120°C). At the same time, it is noted in [1, 8, 10–13] that when electrorheological fluids based on water-activated fillers are heated, the electrorheological effect degenerates. In the researchers' opinion, the reason is that water is easily desorbed from the filler surface; consequently, the number of polarized charges and the force of mutual attraction of particles in the structures of electrorheological fluids change, which causes the electrorheological effect in the system to diminish. Such a difference between the obtained experimental data and those existing is attributable to the different energy states of water molecules in fillers used for creation of electrosensitive hydrated formulations. The strength of the coordination bond of the H_2O molecules and the

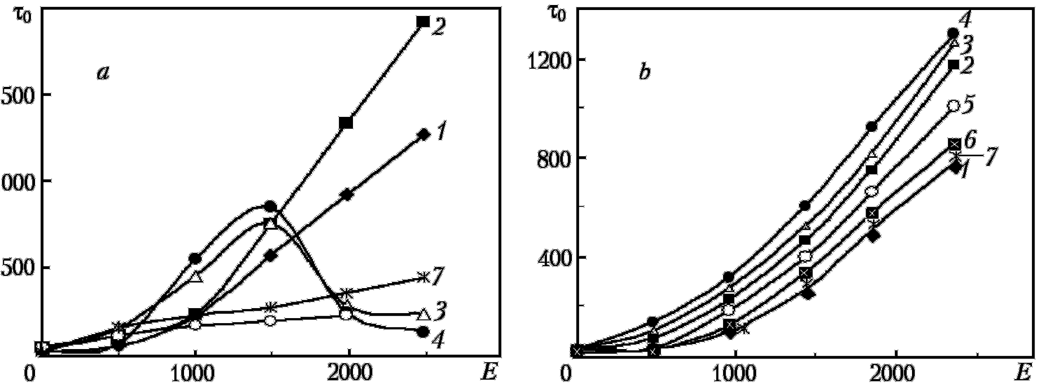

Fig. 4. Quantity τ_0 vs. applied electric field for the electrorheological fluids based on diatomite (a) and on sample No. 2 (b): 1) T = 20; 2) 40; 3) 60; 4) 80; 5) 100, 6) 120, and 7) 20^0C (on heating). τ_0, Pa; E, V/mm.

degree of their protonation will primarily have an effect on the processes of transfer of protons, which determine the surface electrical conduction of this type of fillers. An analysis of investigations [17, 18] of the processes of proton transfer in different interphase phenomena suggests that H^+ whose source are interlayer water molecules protonated in the electric field migrate in the investigated aluminas in the form of pseudoboemite. The protolytic dissociation of water molecules in the electric field and the resulting presence of mobile protons will, in all likelihood, cause H^+ to move to the oxygen atoms in octahedral bunchings. Thus, a chain of hydroxyl groups interacting by means of the hydrogen bond is formed, which points to the substantial role of the proton mechanism in charge transfer. Consequently, electrical conduction is by H^+ transfer between OH groups in this case.

The fact that pseudoboemite-based suspensions show the electrorheological effect at elevated temperatures (see Figs. 3a and 4b) is attributed to the higher thermal stability of water molecules in the composition of this fillers. According to [18], the surface proton conductivity can be represented as

$$\sigma = n\mu e\,.$$

The quantity n will be determined by the concentration of coordination-bonded water molecules and the degree of their protonation. The degree of dissociation of these molecules will be dependent, as has been noted in [18], on the permittivity of the ambient medium and, furthermore, on the temperature. Increase in the temperature contributes to an increase in n and consequently σ, which is confirmed by experimental data (see Figs. 3 and 4). The presence of the maximum on the τ_0–T curves is attributable to the influence of factors having an opposite temperature dependence. It can be assumed, e.g., that increase in the temperature increases n, but the quantity μ that is strongly dependent on the coverage and hydrophilic properties of the surface diminishes.

Of special interest are the data in Fig. 3, according to which there is an optimum content of H_2O in the filler, for which the electrorheological effect is maximum. Increase in the content of, primarily, the adsorbed H_2O molecules having an H bond with the interlayer water in the filler can strongly change μ. Conceivably this might be the reason for the decrease in τ_0 with growth in the content of water in hydrated aluminas (see Fig. 3a). It is seen that the values of τ_0 for the electrorheological fluid based on sample No. 1 (which contains 33.0% H_2O, or 2.78 moles of H_2O, part of which is in the form of aluminum-coordinated OH groups, part in the form of coordination-bound molecules, i.e., interlayer molecules, in the pseudoboemite structure, and part in the form of adsorbed H_2O molecules) are lower than for the electrorheological fluid based on sample No. 2; the fraction of coordination-bonded H_2O molecules in them is equal. Since protolytic dissociation is primarily characteristic of H_2O molecules with strong hydrogen bonds, they are the main source of protons and determine n, whereas μ is substantially dependent on the number of the adsorbed H_2O molecules surrounding the coordination-bound water, i.e., on the coverage of the surface and its properties. It follows that both the adsorbed and interlayer forms of water that are present in the fillers of electrorheological fluids play an important role in the phenomena of polarization and surface electrical conduction.

Conclusions. It has been shown experimentally that electrorheological fluids based on hydrated alumina in the form of pseudoboemite possess thermal stability, preserving high indices of ER activity up to 120^oC. Using pseudoboemite as an example, it has been shown that the presence of superstoichiometric water molecules linked by strong hydrogen bonds and dissociating on exposure to an electric field is the necessary condition for thermal stability of the fillers. The use of such fillers in electrorheological fluids will ensure efficient operation of electrically controlled hydraulic devices with an extended temperature range of application.

NOTATION

E, electric-field strength, V/mm; e, proton charge, C; I, cell current, mA; n, concentration of protons, m^{-3}; T, temperature, $^{\circ}$C; ε, relative deformation, %; φ, rotation angle, rad; μ, mobility of protons, $\mathrm{m}^2/(\mathrm{V{\cdot}sec})$; σ, surface proton conductivity, S/m; τ_0, limiting shear stress, Pa; $\tau_{0E}/\tau_{0E=0}$, relative limiting shear stress.

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