Peculiarities of Particle Polarization in Water Containing Fillers for ERF

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Abstract. In the present paper the experimental rheometric information on the investigation of ERF, based on the water containing fillers, is analyzed and generalized. A mechanism of surface polarization for particles of the dispersed medium is suggested.

Introduction
There are plenty of reports on polarization phenomena in ERF, based on the water containing dispersed phase. However, the question about the nature of the processes with interphase transport of protons, which determines surface electroconductivity of the particles, has still not been answered unambiguously. There are several hypotheses on the mechanism of the surface polarization for colloid systems [1]. It is known [2] that different types of hydroxyl groups are feasible to appear on the surface of hydrated hydroxyl containing compounds. However, the nature of the dominating proton containing groups, their role in the polarization processes on the surface of particles of a dispersed phase of ERF is not clear. Therefore, a further discussion and experimental investigations of these problems are needed.

In the present paper we have analyzed and generalized the experimental rheometric material on the investigation of ERF, based on the water containing fillers, and we suggest the mechanism of surface polarization for particles of the dispersed medium.

1. Materials and methods
The experimental investigation of the rheological properties of ERF has been carried out by means of a rotational viscometer of a coaxial-cylindrical type at room temperature. The measurement of the extreme shear stress \( \tau_0 \) has been carried out by means of a vibrorheometer with coaxial cylinders. As extreme shear stress we have assigned the value of the shear stress, at which the elastic deformations change into the plastic deformations. The measurements have been carried out in the regime of a continuous deformation at a constant rate of change of the deformation in the range of temperatures 20 – 120 °C. As fillers for ERF we have used aluminum and chromium hydrated oxides, obtained by means of sol-gel synthesis. These samples were used for preparation of 40 wt. % suspensions in mineral oil. The total content of H_2O in the samples was determined by means of thermogravimetrically in the polythermal regime by heating up to 850 °C. On the basis of DTA-measurements, the quantity of the different types of water were determined in the following regimes: the structured H_2O (in the form of OH-groups) – in the polythermal regime in the temperature range of 350-520 °C, the
unstructured \text{H}_2\text{O} – in the isothermal regime in the temperature range of 170-350 °C (the interlayer \text{H}_2\text{O}) and 80–170 °C (the adsorbed \text{H}_2\text{O}).

2. Results

A qualitative evaluation of the ER-activity of some fluids (obtained by us and known from literature) on the basis of aqueous dispersed phase of different compositions and preparation process is displayed in table. The studied fillers are nominally divided into two groups: the first one refers to the fillers that are obtained by soaking and keeping of the synthetic and natural compounds in the vapor ambient, namely metal oxides, diatomite and etc., that after drying contain a certain quantity of the adsorbed water (column 1). The second group contains inorganic compounds, synthesized by means of chemical deposition from aqueous solutions of reagents and characterized by a certain chemical, phase, dispersed composition (column 2). The investigated samples represent aluminum and chromium hydrated oxides iffered by the structure, the water content in the form of \text{H}_2\text{O} molecules and OH groups, the nature of bonding of these forms of water, the place of localization of water molecules (in between layers in the crystalline lattice and on the surface of particles). In correspondence with the classification [3] in the hydrated metal oxides two water categories are distinguished: the structural (in form of \text{OH}-groups) and the nonstructural (in form of \text{H}_2\text{O} molecules) in two varieties – the interlayer and the adsorbed water. The presence of the interlayer water is due to the fact that in the interburst space of the lattice of the layered structures of hydrated metal oxides, the water molecules are incorporated, which form a hydrogen bond with hydroxyls. The molecules of the adsorbed water are known to join OH-groups by a hydrogen bond. In particular, we have investigated aluminum hydrated oxides (rhombic \gamma\text{AlOOH} (boehmite), pseudo boehmite, monoclinic \alpha\text{Al(OH)}_3 (baehrite)), and also \text{Cr}_2\text{O}_3 \cdot \text{nH}_2\text{O}. In the structure of boehmite, every \text{Al}^{3+} ion is surrounded by six ions of \text{O}^2-, situated at peaks of octahedrons, linked to each other by edges where they are connected with the peaks, forming the double layers, bonded by hydrogen bonds. Pseudo boehmite comparing to boehmite (\text{AlOOH} or \text{Al}_3\text{O}_2 \cdot \text{nH}_2\text{O}), has a content such as \text{Al}_2\text{O}_3 \cdot 1.5-2.0\text{H}_2\text{O}. The structure of the latter is similar to the structure of boehmite, but is composed of two-dimensional crystals. Super stoichiometrical water in the quantity of 0.5-1 mol is localized in the interlayer space of the structure and is bonded by strong hydrogen bonds. Such water molecules are somewhat deformed and thermally stable. Baehrite and threehydrate of aluminum oxide \alpha\text{Al(OH)}_3 \cdot 3\text{H}_2\text{O} have a monoclinic lattice. The content and conditions of obtaining the modifications of hydrated aluminum oxide are shown in table. X-ray amorphous hydrated chromium oxide, depending on the conditions of its preparation contained a variable quantity of nonstructural, namely, adsorbed \text{H}_2\text{O} (see table). According to the table, the filler, containing only structured \text{H}_2\text{O}, has a low ER-activity. The presence of nonstructural water in the filler leads to their substantial activating. Moreover, the degree of the activation of the filler is probably defined not by the place of localization of \text{H}_2\text{O} molecules, but by their quantity and nature of bonding. Thus, the decrease of the content of adsorbed water in the hydrated chromium oxide leads to the vanishing of ER activity (see the table). Therefore, ERE occurs only due to the presence of adsorbed water, consisting in the composition of hydrated chromium oxide in the same way as in the fluids on their basis, for example, diatomite.

In Figures 1, 2 the dependencies of the relative yield stress on the temperature and the yield stress on the electric field intensity for ERF, based on the samples of two groups (diatomite, pseudo boehmite), are shown. As it follows from Figure 1, the ER-effect for ERF, based on the fillers of two types, is comparable at room temperature. By heating higher than 40 °C, ERE in the fluid, based on diatomite, begins to lower, and at \( T = 80 \) °C is almost vanished. For ERF, based on pseudo boehmite, the growth of \( \tau_0/\tau_0 \) up to 80 °C is seen, than the values of \( \tau_0/\tau_0 \) begin to lower, but even at \( T = 120 \) °C they are higher than that at room temperature.

From figure 2 it is seen that by heating of ERF, based on diatomite, up to 80 °C, the application of the high electric field (more than 1.5 kV/mm) leads to the rapid decrease of the increment of \( \tau_0 \) (curve 3). Moreover, high values of current are seen – 1.2 mA. For ERF on the basis of pseudo boehmite, the values of \( \tau_0 \) at the increase of temperature under all intensities of the electric field are increased. The values of the conductivity current for this sample are not high, which allows us to perform the following heating of the substance.
3. Discussion

Analysis of the obtained experimental and published in the literature data allowed us to suggest the following mechanism of the surface polarization of the particles of water containing fillers. As it has been noted, the fillers of the first group are activated by means of surface saturation by water. Such a method of preparation water containing fillers provides a high filling-in of the surface by water molecules and formation of polymolecular layers of H$_2$O. According to [2], first portions of water are adsorbed by the coordination mechanism. Formed proton ionized molecules of H$_2$O become active centers for subsequent adsorption. At high filling-in degree of the surface, clusters of molecules grow up in the tangential direction with the formation of polymolecular film. Such behavior of adsorption with the appearance of coordination bonds is typical for a number of metal oxides [2]. Transportation of protons in the H$_2$O layers provides the surface proton conductivity of the filler particles. The surface polarization in this case can be due to the film polarization, when charge carriers move only along the surface. Under the constant electric field, the polarization of a dielectric with the conductive continuous film is the same as for the fully conductive particle. Evaluations of the concentration of moving protons performed in [2] give the value of 1-2·10$^{13}$ cm$^{-2}$, which is close to the concentration of coordinationaly bonded water on the SiO$_2$ surface.

### Table. Characteristics of aqueous fillers for ERF

| Method of preparation of the filler | ER-activity of the fluids based on these investigated fillers $^*$ |
|------------------------------------|---------------------------------------------------------------|
| 1 Saturation of materials by H$_2$O | 2 sol-gel synthesis |
| Al$_2$O$_3$, Cr$_2$O$_3$             | ++                                                             |
| SiO$_2$[4]                          | ++                                                             |
| Al$_2$O$_3$.H$_2$O or AlOOH (boehmite) | +                                                             |
| TiO$_2$. NiO, SiO$_2$               | +                                                              |
| Al$_2$O$_3$.1.7-2.0H$_2$O (pseudo boehmite) | +                                                              |
| Al$_2$O$_3$.2.97H$_2$O (baehrite)   | ++                                                             |
| Cr$_2$O$_3$.5.H$_2$O                | +++                                                            |
| Cr$_2$O$_3$.3.H$_2$O                | +++                                                            |
| Al$_2$O$_3$ in the form of fiber [1] | +                                                              |
| Diatomite, cellulose [5]            | +                                                              |

$^*$ - are thermo stable

+++ - high (ratio of shear stress under maximum field to that under no field – from 50 up to 100 and higher); ++ - medium (+ from 10 up to 50); + - low (÷ from 1 up to 10)

### Figures 1. The dependence of the relative yield stress on the temperature at $E = 2.5$ kV/mm

### Figures 2. The dependence of the yield stress on the electric field intensity for ERF, based on the samples of two groups
The second group is the aqueous fillers for ERF, in which water is not absorbed on the surface, but is localized in the interlayer space of the crystalline structure, as it occurs in the case of the hydrates aluminum oxide in the form of pseudo boehmite. According to [3], super stoichiometric water in pseudo boehmite is bonded by a super strong hydrogen bridges in the lattice space of boehmite. Such water molecules, as it is known, are somewhat deformed, thermally stable and as the results of investigation have shown, are activators for the particles of dispersed phase, creating their enhanced conductivity. The appearance of proton conductivity in this case can be explained by the dissociation of \(\text{H}_2\text{O}\) molecules, having strong hydrogen bonds in the electric field and by the formation of protons and OH groups.

The polarization mechanism is probably due to the thermal proton polarization. It is due to the presence, on the volume or on the surface, of the particles the chains of hydroxyl or other ionogenic groups, bonded by hydrogen bonds, by which a migration of protons occurs. Two mechanisms of proton migration are known [1]. According to first one, after applying the electric field, protons of hydroxyl move to the free place between two neighboring atoms of oxygen in the chain of hydroxyl groups and the combination of O…O is moving opposite to the field that provides the consequent reorientation of all OH-groups in one orientation. The second mechanism is due to the fact, that under applying the electric field, a proton from a neighboring hydroxyl group will move to a free place and it will continue until the full reorientation of all OH-groups takes place and dipole moment of the whole chain is changed. However, the explanation of the migration mechanism of protons both by the first and by the second variant of transitions of protons of hydroxyl groups arises many questions. Authors do not indicate the types of OH-groups, participating in the reorientation, their concentration and the condition on the surface of the dispersed phase. On the assumption of a number of investigations of proton processes in various interphase phenomena, we suggest that in the aluminum oxides investigated by us in the form of pseudo boehmite as the filler for ERF, \(\text{H}^+\) migrate, the source of which are protonoionized in the electric field interlayer water molecules. Protolytic dissociation of water molecules in the electric field and the presence of mobile protons due to this, most probably will lead to the transition of \(\text{H}^+\) to the oxygen atoms, situated in octahedron groups. Hence, a chain of hydroxyl groups, interacting through a hydrogen bond, is formed, which indicates the sufficient role of the proton mechanism in charge transfer. Therefore, the electroconductivity in this case will be carried out by \(\text{H}^+\) transfer between OH-groups. The fact that the suspensions on the basis of the fillers of the second type show ER–effect at higher temperatures (see figures 1, 2) is explained by a higher thermal stability of water molecules in the composition of these fillers. The increase of ER-effect in the range of temperatures 60-80 °C is because of the increase in the proton concentration due to the increase of a dissociation constant for water molecules, which depends on the permittivity of the medium and temperature.

4. Conclusions

- Two groups of aqueous fillers for ERF are emphasized, different in the type of nonstructural water in the form of the interlayer or the adsorbed water.
- It is shown, that the ERF, based on the fillers, that containing interlayer water, namely pseudo boehmite – a hydrated aluminum oxide, have a high ER-activity and are thermally stable.
- Based on the generalization of the analysis of our investigations and literature data, a polarization mechanism for the filler containing both adsorbed and interlayer water has been suggested.

References

[1] Korobko E V, Levin M L 2007 Physica-chemical aspects of structuring in ERF. Heterogeneous ER-compositions, (Luikov Heat and Mass Transfer Institute 2007) (Preprint № 2) 61
[2] Golovanova G F, Kvildize V I, Kiselev V F 1977 Nature of the protonodonor centers on the surface of oxides \(\text{SiO}_2\) and \(\text{Al}_2\text{O}_3\) Digest [in Russian] Bonded water in dispersed systems (Moscow: Moscow State University Press), 4 178-209
[3] Chalyi V P 1972 Hydroxides of Metals [in Russian] (Navukova Dumka Press.) 150
[4] Gehin C, Persello J, Charrut D, Cabane B 2004 Electrorheological properties and microstructure of silica suspensions J. of Colloid and Interface Science 273 658-667
[5] Zhang S, Winter W T, Stipanovic A J 2005 Water-activated cellulose-based electrorheological fluids Cellulose 12 135-144