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Abstract

Full Text

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ON THE BEHAVIOR IN AN ELECTRIC FIELD AND THE STABILITY OF NONAQUEOUS PLASTIC DISPERSE SYSTEMS

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In previously published works ([1,2]), using soap greases as an example, electrokinetic phenomena in plastic disperse systems with a hydrocarbon dispersion medium were described. In a constant electric field, phase transfer can occur, leading to a change in the structure and rheological properties of these systems ([3]). An effective method for observing electrokinetic phenomena in plastic systems of the grease type is the examination, in polarized light, of solidified oriented flow structures ([4]). This opens up interesting possibilities for studying the influence of surface-active substances on the structure and electrical properties of plastic systems. Of greatest importance is the search for such surface-active substances as can cause a change in the sign of the charge of the phases in greases. After numerous trials it turned out that this effect is observed when well-soluble organic phosphates in hydrocarbon media are added to certain soap greases.

The principal objects of investigation in the present work were hydrated Ca grease (fatty solidol), Li grease (grease 201), and Na grease (fatty konstaline), which were used in our previously published works. The method of simultaneous observation of changes in the macrostructure of systems and of phase transfer in electric fields is described in ([4]). As the surface-active substance we used the additive to oils DF-1 (a 50% solution of barium dialkyldithiophosphate in oil), kindly provided by P. I. Sanin and described in the literature ([5]). The additive was thoroughly mixed into the greases.

The results of experiments with Ca grease are presented in photographs in Fig. 1. The appearance, in plane-polarized light, of the solidified solidol structure oriented in the flow is shown in Fig. 1a. The arrow indicates the direction in which the grease flowed before it was stopped. After an electric voltage (field gradient 15 kV/cm) was applied to the electrodes (black bands in Fig. 1), after 15 min the picture shown in Fig. 1b was observed. Since a sensitive-tint plate was used to increase contrast, the band of the optically inactive dispersion medium in all photographs has a red color. With time, the band of the dispersion medium at the cathode, formed as a result of electrokinetic phase transfer, widens. The formation of the band of dispersion medium and the compression of the structural framework as a whole are not accompanied by any significant disturbance of the orientation of the particles of the dispersed phase composing it, oriented in the direction of flow. This means that, together with the previously described transfer of individual crystallites and their aggregates in an electric field (^{1}), elastic compression of the entire structural framework takes place, while the processes of change in orientation and transfer of individual particles are of secondary importance. Indeed, after removal of the electric field, an expansion of the zone occupied by the structural framework is observed as a result of its elastic recovery. Hence it follows that in sta-

the structural framework can behave as a single three-dimensional formation with respect not only to mechanical, but also to electrical properties.

As a result of mixing 15% of the additive DF-1 into the grease, recharge of the dispersed phase occurs; this corresponds to the photograph shown in Fig. 1b. This picture (and the photographs shown in Fig. 1d) was obtained in the same way as the photograph in Fig. 1b, i.e., first, under the action of shear deformation, an oriented structure was formed; then, after rapid stopping of the flow, an electric field was applied, the direction of which was perpendicular to the flow lines. The photograph was taken after holding the system in the electric field for 15 min (Fig. 1b and d).

When the additive DF-1 is introduced into the grease, apparently, along with adsorption processes, chemical processes also take place. As a result, the system changes with time. Two days after introduction of 15% of the additive DF-1 into the grease, and 20 min after application of the electric field, compression of the structural framework inside the condenser and the formation of bands of free dispersion medium at both electrodes were recorded. This state of the system is of special interest and therefore will be considered by us in greater detail. Four days after introduction of DF-1, the dispersed phase again acquired a negative charge.

Recharge of the dispersed phase of the grease after introduction of DF-1 occurs only in those cases where the concentration of the additive is above 10%. At lower concentrations, but close to this value (8–9%) of DF-1, the structural framework is compressed in the electric field inside the condenser; the dispersion medium is located at both electrodes. This leads to the supposition that in nonaqueous dispersed systems such a state is possible in which, at the phase boundary, regions bearing opposite charges simultaneously exist. Since exchange reactions between the additive and the soap may occur with time, the nature of the surface of the dispersed phase and, consequently, the system change continuously. In the final result, a system is obtained with a negative charge of the dispersed phase.

Lithium grease 201 practically does not exhibit electrokinetic phenomena. Its properties change sharply under the influence of introducing the additive DF-1. At low concentrations of DF-1 (up to 5%), the dispersed phase of the lithium grease acquires a negative charge. After the introduction of more than 10%

DF-1, the dispersed phase of the grease immediately acquires a positive charge. At intermediate values of DF-1 concentration, the phenomenon of interelectrode compression of the structural framework is observed. As in the cases described with solidol, with time the dispersed phase acquires a negative charge.

Introduction of DF-1 into sodium grease does not change the sign of the charge of the particles of the dispersed phase, but it hinders the formation of solidified structures. After stopping the flow, the structure relaxes, which is detected from the change in dielectric permittivity with time.

As already indicated, the phenomenon of interelectrode compression of the structural framework deserves special attention. The kinetics of this process is presented in Fig. 2. Here photographs a and b relate to observations 2 and 15 min after the field was applied to a calcium grease with a solidified oriented flow structure. First there occurs a slight increase in the concentration of the dispersed phase simultaneously at both electrodes. Following this, interelectrode compression of the structural framework begins, and after a short time clearly delimited layers of the dispersion medium appear at both electrodes. When the electrodes are recharged, a very interesting process is observed: the detachment of portions of the structural framework, compressed in the interelectrode space, that are located close to them, and their simultaneous displacement toward the electrodes. The layers of the dispersion medium are squeezed into the interelectrode space, migrating with time toward the axis

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 1. Effect of the additive DF-1 on the behavior of Ca grease in an electric field
Fig. 2. Kinetics of the process of interelectrode compression of the structure of Ca grease
Fig. 3. Effect of homogenization on the behavior of Ca grease in an electric field
Fig. 4. Effect of heating on birefringence in the solidified flow structure of Ca grease; *a*—at room temperature, *b*—the same system at 50°, *c*—after cooling the system to room temperature

of the solidified flow (Fig. 2 , obtained 5 min after the change in the sign of the electrodes). However, what is most remarkable is that after some time compression of the structural framework in the interelectrode space begins again, and layers of pure dispersion medium are again formed at the electrodes (Fig. 2 , obtained 30 min after the change in the sign of the electrodes). All the processes described show that at a certain concentration of surfactant the solidol becomes a labile system, whose behavior depends not only on its composition but also on the action of the external electric field, in the sense that it can influence the electrical phenomena taking place at the phase boundary.

The phenomenon of interelectrode compression of the disperse phase and the probability of the simultaneous existence of regions on its surface that are different in electrical respect may be important for understanding many structural features of nonaqueous plastic disperse systems, and above all the phenomena of structure formation and stability. This is apparently connected with the very low conductivity of the dispersion medium, which leads to fundamentally different conditions of structure formation in aqueous and nonaqueous highly concentrated disperse systems. The possible coexistence of differently charged regions in the structural framework, and also, probably, on individual particles, makes it possible to suggest that their surface is nonuniform, which should affect the processes of structure formation.

The "isoelectric" state in the systems under consideration must have an entirely different meaning as compared with what is known for aqueous systems. The possibility of the separate coexistence of differently charged regions at the phase boundary in concentrated nonaqueous disperse systems cannot have analogies in aqueous disperse systems, since in the latter case the conductivity factor exerts a powerful influence.

An important observation was made in the systematic study of a solidol that had been stored for a long time. It turned out that a grease which initially had a negative charge of the disperse phase changes with time and, after a long period (more than a year), exhibits the phenomenon of interelectrode compression of the structural framework. This means that, during storage of the grease, under the influence of oxidation, the nature of the surface of the particles of the disperse phase changes and positively charged regions appear on them, causing a rearrangement of the structural framework. This opens up the possibility for denser packing of the particles of the disperse phase under the influence of Brownian motion, which is accompanied by separation of the dispersion medium—syneresis. Thus, in the case of soap greases and other nonaqueous disperse systems in which chemical reactions capable of changing the nature of the surface can occur at the phase boundary, prolonged thixotropic hardening—compression of the structural framework—may have precisely these results as its main cause.

Interesting results were obtained in experiments with calcium grease, which was homogenized under short-term action of high rates of deformation (of the order of 10^6 $\sec^{-1}$). These experiments are illustrated by the photographs presented in Fig. 3. The appearance of the initial oriented grease corresponds to Fig. 1 . When an electric field is applied, a change in the orientation of the particles of the disperse phase occurs at the anode with high speed, spreading into the depth of the system over 4–5 sec (Fig. 3). Simultaneously, electrokinetic transfer of the phases takes place, accompanied by the formation at the cathode of a layer of dispersion medium and by compression of the structural framework at the anode (Fig. 3 , , , obtained respectively after 1, 2.5, and 5 min). The change in the orientation of the particles of the disperse phase at the anode is apparently due to the sharp outflow of dispersion medium from the anode when the field is applied.

Thus, in the present work it has been shown that under the action of an electric field in plastic disperse systems there can occur ob-

···reversible compression of the three-dimensional structural framework. In the presence of surface-active substances, recharging of the dispersed phase is observed in them. At the phase boundary in the systems under consideration there may exist regions charged in different ways. During storage of greases, as a result of their oxidation, the nature of the surface of the particles of the dispersed phase changes, which should have a decisive influence on syneresis.

Heating the solidol to 45–50° causes the disappearance of the solidified stream structure visible in polarized light. However, after the grease is cooled, it appears again. This is shown in Fig. 4.

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REFERENCES CITED

1. Yu. F. Deinega, G. V. Vinogradov, A. M. Vovnenko, *Kolloidn. zhurn.*, **23**, 257 (1961).
2. Yu. F. Deinega, A. M. Vovnenko, *Dokl. AN USSR*, No. 6, 769, 1961; No. 8, 1052 (1961).
3. Yu. F. Deinega, *Dokl. AN USSR*, No. 3, 397 (1962).
4. Yu. F. Deinega, G. V. Vinogradov, *DAN*, **143**, 898 (1962).
5. P. I. Sanin, V. V. Sher, et al., in the collection *Additives to Oils and Fuels*, Moscow, 1961, p. 85.

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