Rheological, spectral, and thermographic methods are widely used in studying the composition, structure, and properties of lubricating greases; in addition, however, dielectric studies are being used to an increasing extent [1-10].

Study of the dielectric properties of greases can provide more detailed information on the grease structure.

In [10] it was shown that, in studying the structurization of disperse systems, an approach offering many advantages is an investigation of the temperature dependence of dielectric constant ($\varepsilon$) over the range of temperatures for structure formation and breakdown; for lithium greases, this range is 20 to 220°C.

In the present work, the material used as the thickening agent (disperse phase) was lithium stearate (StLi) and lithium 12-hydroxystearate (12oStLi), these being the best soaps for use in grease manufacture. The soap concentration was varied from 0.005 to 12.0% by weight; i.e., the study included systems ranging from low-concentration dispersions all the way to lubricating greases. The dispersion media used in this work were the nonpolar naphthenic-paraffinic oil S-220 (GOST 8463-57) and the polar synthetic liquid dioctyl sebacate (DOS, MRTU 05-1249-69). The dispersions were prepared by heating the soap-oil blend to 200-210°C with constant mixing, holding at this temperature for 15 min, and cooling in the cooking vessel to 20°C when slow cooling was desired, or in a 0.6-mm layer in a pan for fast cooling. The temperature dependence of $\varepsilon$ for these products was determined by means of a bridge of the MIE R 577 type and a high-frequency E-7-5a capacitance meter, at frequencies of 1 kHz and 0.6 MHz, respectively. Generators of the G3-33 and G3-34 types were used in determining the frequency dependence of $\varepsilon$. The initial capacitance of the measuring cell at a frequency of 1 kHz was 47 pF, and the accuracy of determination was $±1 \text{ pF}$; at a frequency of 0.6 MHz, the initial capacitance was 52 pF and the accuracy of estimation $±0.2 \text{ pF}$. The error in determining $\varepsilon$ at either frequency, within the range of temperatures investigated, was at most 0.05. The yield stress of the greases was determined in a K-2 plastometer at 20°C (GOST 7143-54). The kinematic viscosity of the soap dispersions was determined at 100°C. The microstructure of the dispersions was studied by means of an ЭМ-7 electron microscope at a magnification of 24,000.

The results of these studies indicate that, for dispersions of StLi in the nonpolar petroleum oil S-220, when soap is added in amounts up to 0.05% by weight, the magnitude and nature of the variation of $\varepsilon$ with temperature $\varepsilon = f(t)$ is hardly any different from that for the pure oil (Fig. 1а, curves 1-3); i.e., we observe a gradual decrease of $\varepsilon$ with temperature due to a greater degree of random thermal motion of the particles. This indicates the absence of any three-dimensional structure in the system, even though the formation of micelles does take place at these concentrations, as indicated by data obtained by electron-microscope analysis of the dispersions (Fig. 2а and 2b). In the field of StLi concentrations from 0.05 to 0.25% by weight, when the temperature is increased to 160°C or more, in contrast to the behavior of the oil, we see a smooth increase in $\varepsilon$ (Fig. 1а, curve 4) due to breakdown of the micellar associates and accumulation of polar particles in the system (see Fig. 2с). At a temperature of 160-170°C and an StLi concentration of 0.25% by weight or more, we observe a sharp increase, i.e., a jump in dielectric constant. This indicates the breakdown of the three-dimensional structure of the disperse system; the concentration and temperature at which this abrupt change in dielectric constant takes place can be used arbitrarily to judge the thickening action of the soap. The lower the soap concentration and the higher the temperature at which we observe an abrupt change in $\varepsilon$, the greater the thickening power of the solid phase.
It is interesting to note that the thermal phase conversions of these lithium greases [11] and soap dispersions do not correspond to the temperatures of abrupt increase in dielectric constant. The lack of any such correlation has also been noted for aluminum soap dispersions [12]. This indicates that the structural conversions in colloidal systems that give sharp changes in $\varepsilon$ are not accompanied by any appreciable heat effects.

Structurization of dispersions depends to a great degree on the type of thickening agent and its polarity. Studies of the initial process of structure formation (with low concentrations of disperse phase) are very important in understanding the peculiar features of grease structure and properties when the greases are prepared with different thickening agents. For example, study of the structurization of 12oStLi in S-220 oil revealed a number of peculiar features of this process and made it possible to compare the thickening effect of 12oStLi with StLi. The introduction of 12oStLi into S-200 oil and an increase in the soap concentration up to 0.25% do not bring about any changes in the nature of the temperature dependence of $\varepsilon$ (see Fig. 1b, curves 1-3). With soap concentrations from 0.25 to 1.0%, we observe a smooth increase in $\varepsilon$ at temperatures above 170°C (see Fig. 1b, curve 4); a jump in $\varepsilon$ appears at a temperature of 150-160°C with a dispersed-phase concentration of 1.0% or more (see Fig. 1b, curves 4-7). Thus, the thickening effect of 12oStLi, which is more polar than the StLi, is found to be considerably lower than that of the lithium stearate in the nonpolar S-220 oil. When the 12oStLi concentration is increased above 1.0%, we also observe the abrupt change in $\varepsilon$ is shifted toward lower temperatures, by 20-30°C.

Fig. 1. Concentration and temperature dependence of dielectric constant of soap dispersions in S-220 oil. a) Lithium stearate: 1) 0%; 2) 0.01%; 3) 0.05%; 4) 0.25%; 5) 1.0%; 6) 8.0%; 7) 12.0%. b) Lithium 12-hydroxy stearate: 1) 0%; 2) 0.05%; 3) 0.25%; 4) 1.0%; 5) 2.0%; 6) 6.0%; 7) 10.0%.

Fig. 2. Microstructure of lithium stearate dispersion in S-220 oil: a) 0.005%; b) 0.01%; c) 0.05%; d) 0.25%.