DIAGNOSTICS OF MESOMORPHIC STATES OF COMPOSITE LUBRICANTS BY THEIR TEMPERATURE-DEPENDENT VISCOSITIES

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The procedure and results of investigations of mesomorphic-state composite lubricants by optical and viscosimetric methods are presented.

A large role in forming the operating characteristics of a lubricant is assigned to functional additives, which create a mesomorphic structure in the presence of solvents. A study of the basic tribological and electrophysical characteristics of such composites has shown that the latter form a liquid-crystalline structure on a surface of metals as well [1].

Preparation and application of composite lubricants is connected with the dissolution of additives in them, which get dispersed to a molecular level. Molecules of the additives are uniformly distributed in a solvent to form homogeneous stable systems.

The solvent molecules penetrate into a swelling additive. A nondense structure of the additive consisting of filamentary and curved macromolecules entangled with each other, favors the penetration. Molecules of a low-molecular liquid, penetrating deep down, fill a free space between the additive molecules, thus displacing them from each other and weakening their interaction. The formed "gaps" are being occupied with the next molecules of the solvent, the swollen macromolecules of the additive begin to separate and pass into a solution.

This process of low-molecular liquid absorption of a solvent occurs only at a certain temperature which has been called "a penetration point." Dissolution is a spontaneous process which takes place at contact of a dissolved substance with a solvent and is described, as known, by a differential equation of the form

$$\frac{dx}{dt} = k(P - x), \tag{1}$$

where P is the amount of a substance providing a saturated solution; t is the dissolution time; x is the dissolved substance; k is the empirical coefficient.

The present paper offers the results of investigations of new composite lubricants by optical and viscosimetric methods. The temporary and quantitative characteristics of dissolution of a test additive were determined on a LMF-72M photometer. The time of complete dissolution of the test substance was determined by the stabilization moment of a transmission coefficient. Simultaneously, determination was made of temperature characteristics. As an additive, cholesteryl palmitate dissolved in petrolatum was used.

It is established that for the given substance to be dissolved "the penetration point" lies within 345 to 347 K, and saturation of the homogeneous-state solution occurs at a concentration of 4.2%. From the experimental plot of a proportionally coefficient k vs concentration C, % (Fig. 1) an empirical formula is obtained to calculate the optimal time of additive dissolution, the estimation of which is required to work out a process of composite lubricant production:

$$t = \frac{1}{k} \ln \left(1 - \frac{x}{4,2}\right). \tag{2}$$

The obtained parameters are to be maintained in the production process in order to achieve a mesomorphic state of the medium. A transition into a mesomorphic state radically changes the properties of the obtained composites and, as a consequence, their physical and technical characteristics.

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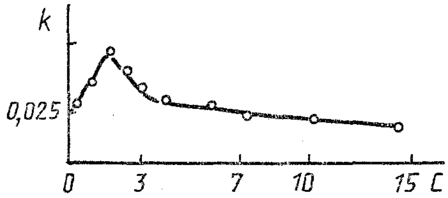

Fig. 1. Coefficient k vs additive concentration. C, %.

For the mesomorphic-state media, of importance are orientational effects: a change in the direction of the major molecule axis under an influence of a surrounding medium, i.e., the anisotropy of optical and viscous properties.

An influence of the medium on the orientation of molecules in a volume was evaluated in quartz cells by a LMF-72M photometer after preparing composite lubricants of different concentrations. Measurement was made of a transmittance of monochromatic light at different wavelengths as a function of cell dimensions. In order to obtain a planar structure oriented along light beam propagation, a cell surface was subjected to mechanical treatment [2].

The obtained data have shown that for the 50.14 mm long cell, a decrease in the concentration from 2 to 0.2% results in an increase of the transmittance up to 0.95 of the pure oil transmittance assumed to be unity. With decreasing the cell length to 5.14 mm, the transmittance for the solution with a cholesteryl palminate concentration of 1.25% at a wavelength of 480 μm has undergone a 1.1-fold increase, as compared with pure oil, while at other wavelengths there is observed absorption. At an additive concentration of 0.25%, light intensity has increased to include the wavelengths 400-540 μm and at 480 μm it has attained a 1.6-fold increase. Thus, the effect of selective light reflection on a planar structure is established. This allows, without quantitative analysis of the results, a qualitative statement about the medium as a system with optical properties of planar cholesteryl layers having an ordered structure at a wavelength of 5.14 mm at an additive concentration from 0.25 to 1.25% and being consistent with features of the similar systems discussed in [3].

However, these investigations only permit classification of the obtained composite lubricant but do not permit evaluation of its technical capabilities.

A viscosity is one of the important technical characteristics of a liquid. It is to be taken into consideration in different engineering calculations, e.g., calculation of energy consumed for stirring and displacement of a liquid. By the viscosity, one may judge the efficiency and technical applicability of composites regarding specific operation conditions, for instance, evaluation of lubricating properties at specified friction conditions, the capability to ensure normal operation conditions at an elevated temperature, etc.

To calculate lubrication regimes, it is necessary to determine the viscosity of composite lubricants as a function of their concentration and temperature. We have obtained these dependences by using a rotary viscosimeter, the cell of which is temperature-controlled. A temperature has been controlled at the inlet and outlet of the measurement zone.

The desired quantities, i.e., the plastic viscosity η and the limiting dynamic shear stress τ were calculated from formulas which, after determination of the viscosimeter constants, have the form

$$\eta = 697\,(\varphi_2 - \varphi_1)/(n_2 - n_1), \tag{3}$$

$$\tau = 3{,}444\,[\varphi_2 - n_2\,(\varphi_2 - \varphi_1)/(n_2 - n_1)], \tag{4}$$

where φ_1 is the angle of scale rotation measured at a speed of rotation n_1; φ_2 is the angle measured at n_2, here $n_2 > n_1$.

For comparison, we used stearic acid dissolvable in petrolatum and giving a smectic structure in solution [4].

To determine the dissolution effect on composite properties by a viscosimeter, we incorporated one part of the additive into 99 parts of petrolatum and the mixture was poured into a measurement cell at room temperature.

During measurements, the viscosity and its change due to temperature were determined. At a temperature equal to "the penetration point," the mixture had been kept for the time calculated by formula (2) to obtain a homogeneous system and then we continued viscosity measurements.

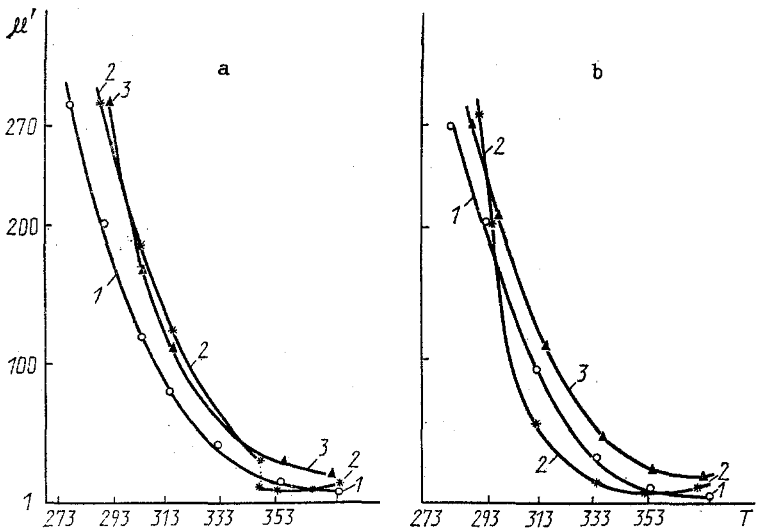

Fig. 2. Plastic viscosity of composite lubricants vs temperature during (a) and after dissolution of the additives (b): 1) petrolatum; 2) petrolatum + cholesterol palmitate; 3) petrolatum + stearic acid. μ', Pa·sec; T, K.

Inspection of the results in Fig. 2a reveals that the viscosity of composites 2 and 3 is higher than that of the petrolatum solvent till the dissolution temperature. Then the viscosity of composite 3 decreases but is still higher than the solvent viscosity. The situation is different in the case of system 1 having a planar structure. Its viscosity is lower than that of the solvent till 366 K, then it decreases to exceed the solvent viscosity. Viscosity curves 2 and 3 are seen to approach the petrolatum viscosity curve till the dissolution temperature which is attributed to reducing the modular deposits and particles of the additives to smaller fractions as a result of stirring the medium.

Figure 2b shows the viscosity of composite lubricants vs temperature but after dissolution in the temperature range 283-380 K. These plots illustrate that the viscosity of composite lubricant 2 is even higher at first than its counterpart of composite lubricants 3, then it decreases, due to temperature, even more actively than that of the remaining samples and at T = 297 K it crosses the solvent viscosity curve, goes below it till a temperature of 366 K, then ascends, thus exceeding the solvent viscosity values.

Proceeding from the basic properties and characteristics of the phase state of liquid-crystal materials, there are grounds for believing that at 283 K the composite material loses its mesomorphic properties. Then upon heating, the material changes to a smectic phase since a viscosity value lies between those of composite 3 and the solvent. A further increase of the temperature makes the structure of composite 2 rearrange into the planar one, i.e. causes the parallel displacement of layers relative to the surface. When being displaced, they entrain the liquid – the solvent and thus reduce the system viscosity.

However, the composite may be in a mesomorphic state (the latter includes smectic, nematic, and cholesteric phases) only at certain temperatures, then it converts to an isotropic liquid, the main feature of which is an increase of the medium viscosity which has been observed in the composite 3 at T = 374 K.

Investigation of the concentration effect of a liquid-crystal additive on viscous properties of a composite lubricant has shown that at each concentration there is a peculiar dependence of the composite lubricant viscosity on the temperature. Therefore we have conducted viscosity measurements as a function of the concentration at different temperatures.

Their analysis shows that the additive begins to influence the composite viscosity when its concentration in the composite is not less than 0.01%. Examination on a disk type friction machine – a ring has demonstrated that a friction coefficient of such a composite also decreases by 10% as compared to that of pure petrolatum. A minimum viscosity is observed for a homogeneous composition with a concentration of 0.75%, with a further concentration increase, the viscosity increases. At a concentration in excess of 2% the composite transforms into a smectic phase, i.e., the viscosity becomes higher than the solvent viscosity. At a concentration over 4.2%, the composite converts to a heterogeneous system and becomes thickened to a plastic state.

It is established [1] that friction characteristics of a friction unit are specified by a liquid-crystalline state of boundary layers of a lubricant and properties of its mesomorphic structure. Such structures in a solution provide a minimum thickness of a boundary layer up to $1 \cdot 10^2$ μm and a binding energy up to 10 eV.

The performance of the composite lubricants is explained by the ability of molecules of the mesomorphic-state additive to self-orientate and to self-organize (structurization) with the subsequent orientation by major axes along microrelief grooves and for displacement – in the direction of motion. For the investigated mixtures, a change has been observed not only in the upper [5] temperature phase transition due to the state of the surrounding medium but also in the lower transition, which depends on the composition, varies by 10 to 15 K.

The obtained results show that the procedure developed permits study of the phase transitions of the test composite lubricants by the experimental plots of viscosity vs temperature in disperse, mesomorphic, and isotropic states, and the mesomorphic state characteristics by viscosity curves. It offers the possibility to predict the properties of composites under development and the spheres of their applicability.

Diagnostics of the properties of mesomorphic composites by temperatures dependences of their viscosities makes it possible to classify the condition both of transparent and opaque composite materials.

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