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LIQUID CRYSTALS AS AN OBJECT AND MEANS OF TRIBOLOGICAL INVESTIGATIONS

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Abstract

The unique properties of liquid crystals (LC) have conditioned their extensive use just as in research, so for practical purposes. Lubricating properties (antifrictional, wear resistance) of LC are displayed within the temperature range of the existence of the liquid-crystalline state (mesophase) that can be regulated via creating eutectic mixtures of LC of one and the same class e.g., cholesterol ones (CLC). A combination of CLC with so-called orientants (substances of a similar structure entering the orientation order of CLC and showing strong adsorptive activity) elevates considerably their antiseizure characteristics. Investigations of the processes occurring during friction of solids in the presence of LC have disclosed interactions in the lubricating media and between their components and contact surfaces, conditions that bring about boundary layers and their parameters, and so on. Studies of boundary layers in CC containing LC by electrophysical methods have assisted in forecasting their triboengineering properties proceeding from the parameters of contact conductivity of the metal surfaces. The work quotes some examples of using LC as an object of triboengineering purposes and a tool of tribological investigations.

***Keywords**: lubricating materials, tribological properties, contact resistance, additives, cholesteric liquid crystals*

Introduction

A predetermining factor of the boundary friction regime is the interaction between lubricant components and contacting surfaces, which results in formation of a structure of one or another ordering. Additives of different nature, activity, structure and mechanism are intended for and improvement of triboengineering characteristics of lubricating media. Liquid crystals of cholesteric type form a separate class of additives. When interacting with the surface and forming layered structures of various ordering degree and possessing low shear resistance but high compressive one, these additives are able to promptly respond to the changes in friction conditions, optimize thickness of the boundary layer and temperature in the friction zone. The uniqueness of the cholesteric liquid crystals (CLC) is supported by their presence in living organisms. CLC contained in biological lubricants may maintain normal functioning of joints under severe loads and velocities with abnormally low friction coefficient [1]. Biological tribosystems may serve an example for many engineering solutions [2].

Boundary layers parameters and integrity of their structure (mechanical strength) present a specific interest in forecasting tribological properties of lubricating materials at the stage of their designing. Electrophysical methods using probes are in this respect most adequate for estimation of the conductivity of point contacts of the boundary layers adjacent to the metal surface. The reported data in the field of designing lubricating materials with various additives visualizes a simple regularity, i.e. the less the contact conductivity (the contact resistance being higher), the thicker the boundary layers and the higher their protecting properties [3]. The use of liquid crystals in electrophysical research methods assisted in recording new regularities in formation of the boundary lubricating layers and developing liquid-crystalline additives for lubricants of different purposes.

Investigation objects and methods

The objects of investigations were the CLC with various mesophase range, as well as their eutectic mixtures and blends with other substances yielding a synergetic effect when used as additives for lubricating materials (LM). The initial LM was Vaseline oil (VO) whose inertness made it possible to exclude or to minimize participation of its components in the formation of boundary layers.

The tribological investigations were carried out following the roller-bush and roller-spherical roller geometries on the SMT friction machine fit with a system of contact resistance recording.

Experimental results and discussion

The mechanism of CLC affect as lubricant additives is closely related to the structure of molecules and their thermodynamic properties. The geometrical factor (rod-like shape) of the molecules with a slight dipolar moment realizes a parallel (planar) relative to the surface orientation of the molecular layer as a most beneficial in terms of the energy, which leads to some evening-out of the microrelief of the rough surface. The LM containing CLC as additives operate at the initial stage of interaction between contacting bodies in the run-in regime. Further, the structure of the boundary layer is formed under the action of the intermolecular forces of the additive. It represents monomolecular layers, which overlap so that the axis of each subsequent layer is turned by some angle. Depending on the value and direction of the mechanical shear the structural changes may minimize losses at friction. The capability of forming highly oriented structures is displayed by CLC only within a certain temperature range (mesophase range) that matches the range of the efficient lubricating properties of these materials used as additives (Fig. 1).

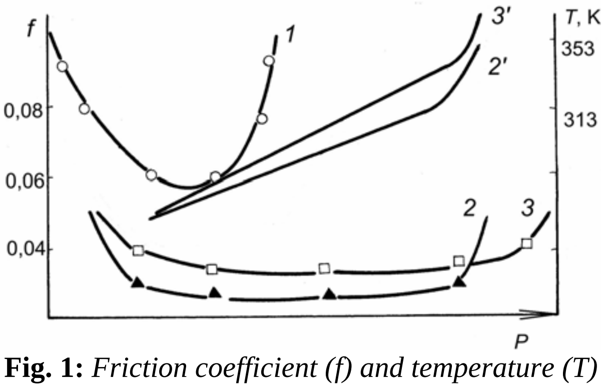

Fig. 1: *Friction coefficient (f) and temperature (T) dependence on specific load (P) on the steel-steel friction pair in: 1 – VO; VO solution with 1% of: 2, 2′ – cholesterol oleate; 3, 3′ – cholesterol stearate*

When speaking about the efficient lubricating properties of materials, we mean low wear, friction coefficient and temperature in the friction zone. Since every CLC has an intrinsic mesophase range not exceeding sometimes 10 °C, so the task of using CLC in practice as additives presupposes the search for the possibilities of producing the substances with a wider range of efficient properties. Composing of the blends with individual CLC differed in the mesophase range has resulted in eutectics with an expanded range and lower friction parameters (Fig. 2).

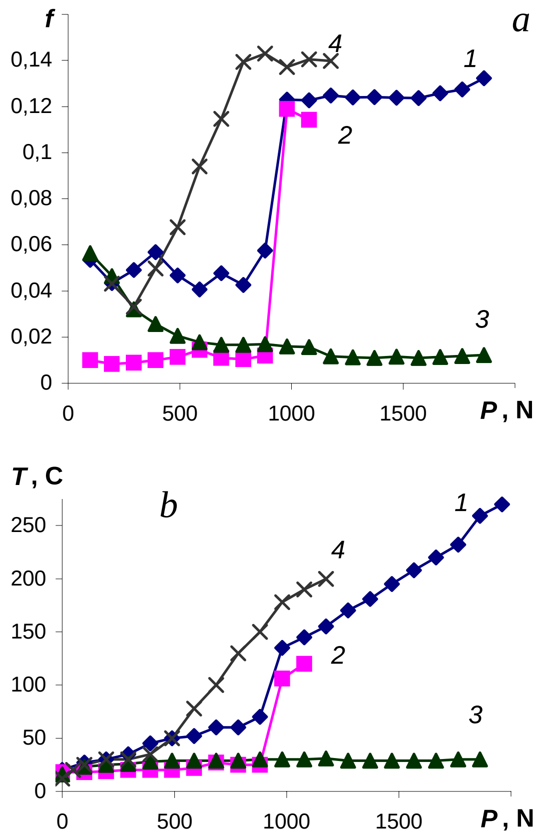

Fig. 2: *Friction coefficient (f) and temperature (T) (a) versus load (N) (b) for lubrication media: 1 – VO + X-20; 2 – VO + X-1; 3 – VO + X-1+X-20; 4 – VO*

The investigation results and usage of CLC additives in mineral oils have confirmed perfect antifrictional and wear-resistant properties of the LM.

Mechanical strength of the structures formed by CLC (endurance of normal stresses about 5-10 MPa) is attributed to their incompressibility. However, in severe friction conditions (high loads and velocities) CLC turn inefficient because of low adsorptive activity and weak cohesion of the boundary layer molecules to the contact bodies surface. This is, probably, because of the tearing off of such films prior to the formation of the boundary layer state by the LC. In this case, it's justified to use so-called orientants, i.e. the substances with similar to CLC and incorporating into their structural order. For instance, cholesterol or oleic acid for the CLC as the cholesterol oleate. The structure of the boundary layer is built in this case by the principle "similar with a similar one". Adhesion to the metal surface is ensured by cholesterol or oleic acid as a more adsorption active matter (having active functional groups). In the case with cholesterol, the cholesteric nucleus contacts only a cholesteric nucleus of the cholesterol oleate, while the hydrocarbon chain of oleic acid – with the hydrocarbon chain of cholesterol oleate, which is followed by the formation of layered structures keeping to the laws of chirality, typical of CLC. The practical result of using orientants is the improvement of antiscuff properties of LM incorporating the described complex additives (oleic acid + cholesterol oleate or cholesterol + cholesterol oleate) (Fig. 3).

A compromise combination of antifrictional, antiwear and antiscuff properties of CLC serves the base for their efficient use as additives to different-purpose LM. Notice that even minimal addition of CLC into the coolants on water base raise their triboengineering parameters till the level of the oil-based process lubricants (Fig. 3). In this case, stability of the coolant emulsion is provided by the ultrasound dispersion of CLC in a hydrogel solution [4].

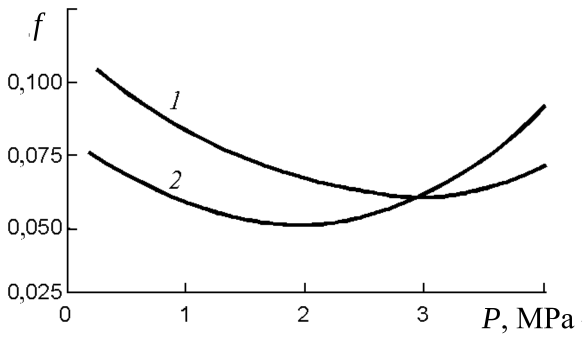

Fig. 3: *Friction coefficient (f) versus specific load (P) for the metal-metal friction pair using: 1 – oil MS-20; 2 – process lubricant based on hydrogel with LC additives*

A combination of hydrogel solution with CLC is intrinsic for biological systems. The articular lubricant is known to contain a hydrogel solution of hyaluronic acid and the eutectic mixture of CLC with the mesophase temperature about 20-45 °C. The medications created via simulation are adequately reproducing the articular lubricant properties, so can be used for treating diseases, pathologies and traumas of joints to replenish its lack or for full substitution (Fig. 4) [5].

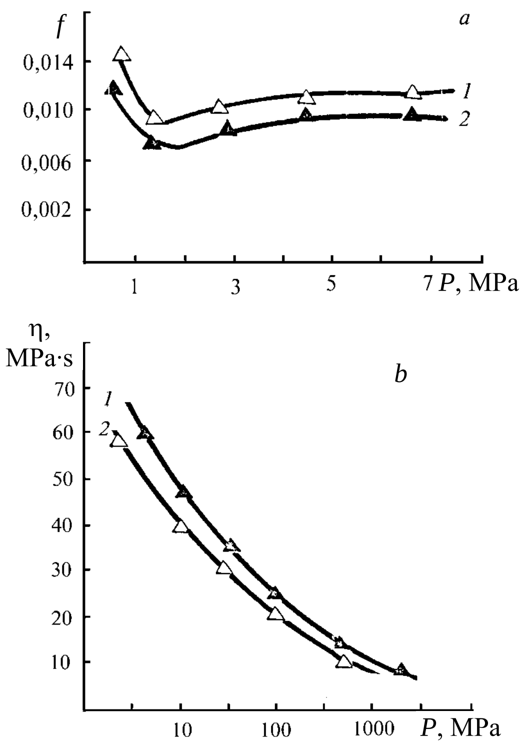

Fig. 4: *Friction coefficient (f) versus specific load (P) (a), and viscosity (η) versus shear rate (D) (b) for: 1 – biological lubricant (synovial fluid); 2 – developed medication Diasynol for treating joints*

The use of CLC as a tool for studying boundary layers was aimed at establishing the validity of probe methods in forecasting triboengineering properties of LM in terms of their contact conductivity. According to the data presented in [3], high contact resistance of boundary layers may be a proof to their greater thickness, less probability of the metal contact and higher load-bearing capacity of the friction joint. Nevertheless, the CLC have exhibited an ambiguous behavior of the relation between electrophysical and tribological parameters of the boundary layers.

To determine the role of CLC in formation of the boundary layers we compared the data on contact conductivity of the dry and lubricated contacts. For the degreased metal surfaces the contact resistance is in fact the resistance of oxide films, whereas for the lubricated contact its is the resistance of the physically or chemisorbed layers resulted from the competing effect of CLC molecules and the base oil with the surface. Since the adsorptive activity of paraffin molecules of the oil is extremely low, their participation in the formation of boundary layers is the minimal.

The results presented in Table 1 visualize that the contact resistance reduction for the VO with increasing load may be attributed to squeezing of the weak physically sorbed boundary layers of hydrocarbons from the contact zone. Diminished friction coefficient may be a result of raised temperature and the formation of oxidized forms being a kind of antifrictional additives. Operation of the friction joint under a 450 N load for an hour leads to increasing contact resistance and further reduction of the friction coefficient, which is a confirmation of the forming oxidized hydrocarbons and arising boundary layers.

Table 1. Contact resistance *R* and friction coefficient *f* versus load *P* for different lubricating media

	Dry friction	VO		X - 6		X - 3		X - 7		T – 20	
P, N	*R*, mΩ	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*
20	2	45	0.840	6	0.210	4	0.420	50	0.420	38	0.315
100	1	25	0.252	5	0.084	7	0.126	48	0.126	34	0.084
150	0.50	17	0.210	5	0.060	10	0.112	45	0.126	30	0.056
220	0.10	15	0.153	5	0.040	13	0.114	43	0.076	20	0.057
280	0.01	14	0.142	7	0.030	14	0.09	40	0.076	18	0.060
350	0	13	0.132	7	0.040	12	0.084	38	0.084	17	0.060
410	0	7	0.128	7	0.036	10	0.082	36	0.072	15	0.056
480	0	5	0.114	7	0.031	7	0.08	35	0.070	13	0.052

Table 2. Contact resistance *R* and friction coefficient *f* versus time *t* for different lubricating media

	VO		X - 6		X - 3		X - 7		T - 20	
t, min	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*	*R*, mΩ	*f*
0	6	0.114	7	0.031	7	0.080	35	0.070	13	0.053
5	50	0.113	3	0.057	8	0.075	50	0.070	25	0.050
10	250	0.101	4	0.044	9	0.070	60	0.068	35	0.050
15	370	0.096	5	0.040	10	0.068	70	0.065	40	0.040
20	650	0.087	5	0.035	10	0.065	140	0.060	45	0.031
25	650	0.079	5	0.040	9	0.064	180	0.057	50	0.026
30	650	0.085	6	0.040	8	0.064	200	0.052	50	0.026

As for the LM with CLC additives, the stepwise load increase doesn't effect noticeably the contact resistance but the friction coefficient lowers and remains stable low. The investigations in the variation kinetics of the friction coefficient and contact resistance of the friction unit operating under 480 N during 30 min have shown that in the first case the contact resistance is preserved at one level (for CLC of X-6 and X-3 grades), while in the second case it increases insignificantly (for T-20), and augments as much as 6 times in the third one (for X-7). During the studies rather low friction coefficients were recorded (see Tables 1 and 2). Named results have brought us to a conclusion that a liquid-crystalline state of the boundary layers is realized for the X-6, X-3, X-7 T-20 additives. They also prove that other LM components participate in the formation of the boundary layers (for X-7 and T-20) too.

Conclusions

1. CLC represent the efficient antifrictional and antiwear additives for different-purpose LM.
2. It's expedient to use eutectic mixture for lowering temperature in the contact zone and expanding temperature range of service characteristics of LM. To improve bearing capacity of the friction joints it's recommended to employ CLC compositions with so-called orientants (substances with similar structure but higher adsorptive activity) as additives to LM.
3. CLC can be sued as multifunctional additives for LM of biological and technical designations on the water base. The emulsion stability is ensured in this case by the use of hydrogels.
4. The contact resistance magnitude and its dynamics are the informative characteristics for the probe technique used to forecast triboengineering properties of LM. They turn useful in defining the interaction mechanism between the additive and metal surface, the range of efficient properties and, consequently, the field of LM application.
5. The variation regularities of the contact resistance with load increase for the LM with CLC additives are a proof to the formation of thinner boundary layers but having higher efficiency as opposed to the base oil. This is confirmed by the stable low friction coefficient, temperature drop in the contact zone and improved antiscuff resistance.

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