ISSN 1068-3666, Journal of Friction and Wear, 2021, Vol. 42, No. 1, pp. 7–10. © Allerton Press, Inc., 2021.
Russian Text © The Author(s), 2021, published in Trenie i Iznos, 2021, Vol. 42, No. 1, pp. 13–23.

Tribological Characteristics of Chemically Inactive Surfaces in Lubricants Doped with Cholesterol and Fatty Acid Compounds

S. F. Ermakov[a, *], A. P. Sychev[b], I. V. Kolesnikov[c], M. V. Boiko[c], A. A. Sychev[c], S. I. Sokolov[a], and A. Yu. Kravchenko[a]

[a] *Francisk Skorina Gomel State University, Gomel, 246019 Belarus*
[b] *Southern Science Center, Russian Academy of Sciences, Rostov-on-Don, 344090 Russia*
[c] *Rostov State University of Lines of Communication, Rostov-on-Don, 344038 Russia*
**e-mail: ermakov@gsu.by*

Received July 14, 2020; revised October 15, 2020; accepted November 5, 2020

Abstract—It is found that in inactivated vaseline oil, with the addition of oleic acid, the glass samples characterized by the destruction of the contacting surfaces and a significant increase in the coefficient of friction are set almost at the same load of 0.9 to 1.2 MPa. The addition of liquid-crystal cholesterol compounds to an inactivated lubricant during the friction of chemically inactive surfaces (glass) leads not only to a decrease in the coefficient of friction but also to an increase in the load capacity. For example, an additive of 3.0 wt % of the oleic acid cholesterol ester in vaseline oil increases the loading capacity by six to seven times when the glass is rubbed against the glass compared to the medium containing oleic acid. At the same time, using scanning electron microscopy and profilometry at loads of more than 4 MPa, the formation of microgrooves on the rubbing surfaces, which do not affect the characteristics and stability of friction, is established. The results obtained can be effectively used in the friction and processing of chemically inactive surfaces, such as glass, ruby, and diamond in the glass, watch, and diamond industries.

Keywords: chemically inactive surface, tribological properties, lubricating compositions, liquid-crystal compounds of cholesterol, fatty acids

DOI: 10.3103/S1068366621010025

INTRODUCTION

Analysis of the published data in the field of tribology shows that at this stage, the improvement of lubricants is possible only at a qualitatively new level. The properties of traditionally used lubricants do not always fully meet the requirements of modern industry, transport, and other industries [1]. Lubricants and other related products are required containing new highly effective compounds as lubricants or additives [2–5]. Research in this direction is inextricably linked with the solution of the three main problems in the field of the lubrication of solids: (1) identifying the type and characteristics of the molecules of the lubricating medium that can effectively participate in the contact zone during sliding; (2) the establishment of factors influencing the orienting ability of lubricant and additive molecules in the contact area; (3) elucidation of the role of surfaces in the structuring of boundary layers in thin lubricating films [5].

In recent years, the synergistic features of the effect of the lubricating interaction between the lubricant's ingredients are increasingly related to the formation of compact and stable boundary films consisting of mixed adsorbed layers and complex structures formed directly in the process of frictional interaction [6]. It was found that the structure of lubricating films formed on metal friction surfaces affects the lubricating properties and is controlled by the balance of the chemical interaction between the additives, base oil, and surface [7]. An analysis of the studies on the boundary friction of metals in the presence of surfactants shows that the friction of a surfactant molecule with an active carboxyl group is most effectively reduced, i.e., molecules of fatty acids (oleic, stearic, etc.). As a result of the chemical reaction with the friction surface, they form structurally ordered metallic soaps of a smectic structure [8, 9]. When rubbing chemically inactive surfaces, such surfactants are ineffective [8]. At the same time, the experimental data obtained in recent years suggest that the use as additives of substances that form strong bonds with the friction surface regardless of their nature, in particular, liquid-crystalline cholesterol compounds, is promising. For example, it is well known that such compounds contribute to the formation on the friction surfaces of biological objects of firmly adhered adsorption layers of natural joint lubrication—synovial fluid [10]. In other words, it can be assumed that, due to these properties, the interfacial layers of the choles-

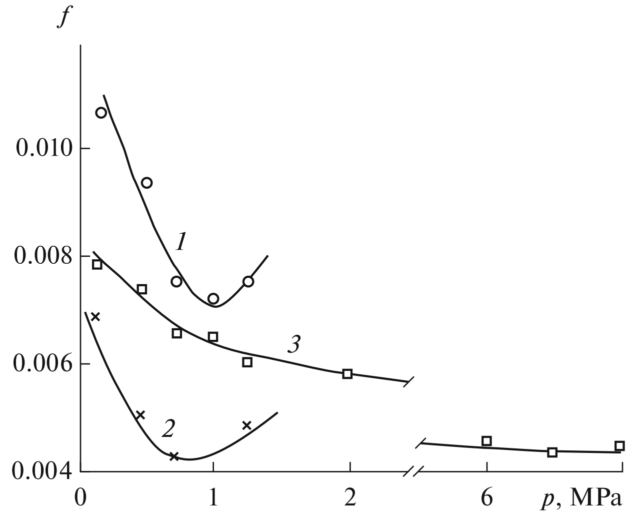

Fig. 1. Dependence of the coefficient of friction on the load for the glass–glass pair when lubricated with vaseline oil (*1*), with an addition of 3 wt % oleic acid (*2*), with an addition of 3 wt % of oleic acid of cholesterol ester (*3*).

teric structure should have a higher screening effect than the interfacial layers of the smectic structure, regardless of the nature of the rubbing bodies, in particular, during the frictional interaction of chemically inactive surfaces.

This study aims to establish the regularities of the influence of additives of cholesterol and fatty acid compounds in lubricants on the friction of chemically inactive tribopairs.

MATERIALS AND METHODS

Apart from the surfaces of gold, platinum, nickel, and chromium, the glass surface is also related to chemically inactive surfaces [8, 10]. The latter was used in our experiments. Moreover, the studies were carried out on a homogeneous glass–glass friction pair. Vaseline oil, which is inactive to the test materials, as well as its mixtures with oleic acid (fatty acid) and its derivative, cholesteryl ester of oleic acid (liquid crystal compound of cholesterol), was chosen as the lubricant. In order to uniformly distribute the introduced additives, the mixtures were homogenized before testing using an ultrasonic disperser.

The frictional interaction was investigated on a tribometer, which implements the friction of the end face of three cylinders against a disk. The experiment was carried out as follows. Glass finger samples were brought into contact with the bottom surface of Petri dishes with a diameter of 100 mm rotating at a speed of 0.1 m/s and that were filled with a lubricating medium. A load was applied and a stable value of the friction force was recorded. Then the load was increased by one step and the stable value of the friction force was again recorded. The limiting value of the specific load on the samples was determined by a significant increase in the friction force due to the seizure of the rubbing surfaces, the excess of which above a certain value led to the automatic shutdown of the tribometer with the cessation of the movement of the samples in contact. The latter contributed to the preservation of the seizure areas in their original form, and, therefore, provided the possibility of studying the nature of their destruction, for example, using optical polarizing microscopy, scanning electron microscopy (SEM), or profilometry. IR spectroscopic studies of lubricants doped with cholesterol and fatty acid compounds before and after the frictional interaction of chemically inactive friction surfaces were performed using a VERTEX 70 FT-IR spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the results of a study of the frictional interaction of a glass–glass pair under the conditions of using various lubricants. Analysis of the obtained dependences shows that in inactive vaseline oil and with the addition of oleic acid, the setting of glass samples, characterized by a significant increase in the friction coefficient, occurs practically at the same load of 0.9 to 1.2 MPa.

The friction process in vaseline oil with the addition of oleic acid is accompanied by the visually observed formation of a film of oleic acid on the friction track, despite the fact that the lubricant was homogenized before the start of the experiment. Consequently, the decrease in the friction force in a lubricating medium with the addition of oleic acid is due to the separation of dynamically contacting surfaces by the polymolecular layers of oleic acid. The low load capacity of such a lubricant is due to the low energy of the interaction of oleic acid with the glass surface [8], apparently close to the energy of interaction of the molecules of vaseline oil with the same surface. Glass, according to [8], under certain conditions is not prone to the chemisorption of oleic acid molecules. Therefore, oleic acid molecules interact with each other with carboxyl groups to form dimers. The dimerized oleic acid molecules are to some extent similar to the molecules of liquid paraffin with their hydrocarbon radicals. Apparently, this similarity determines the similarity of their lubricating properties with respect to glass surfaces.

This assumption is also supported by the results of the study of friction surfaces obtained by SEM and profilometry, according to which the nature of destruction of rubbing surfaces in these cases is the same as in dry friction, i.e., it is related to the deep chipping of glass (Figs. 2a–2c, 3a–3c).

The addition of liquid crystal cholesterol compounds, for example, cholesteryl ester of oleic acid, to an inactive lubricating medium during the friction of

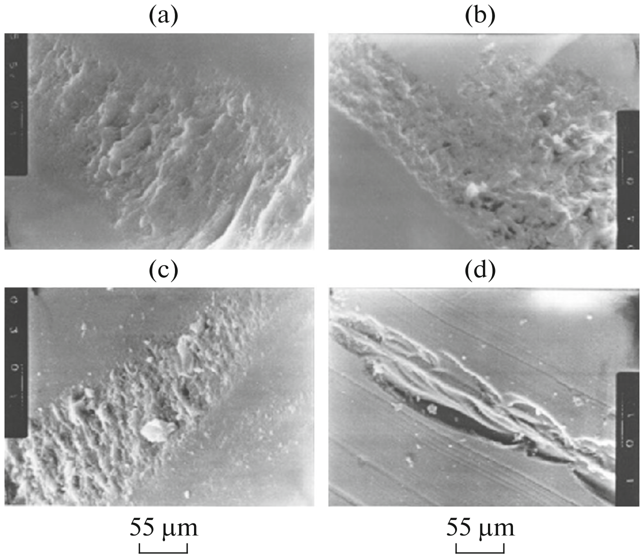

Fig. 2. Friction surfaces of glass samples: (a) without lubrication; (b) when lubricated with vaseline oil; (c) with an additive of 3 wt % of oleic acid; (d) with an addition of 3 wt % of oleic acid of cholesterol ester; (a, b, c) p = 1.2 MPa; (d) p = 7.0 MPa; V = 0.1 m/s.

chemically inactive surfaces leads not only to a decrease in the friction coefficient but also to an increase in load capacity. For example, an additive of 3.0 wt % of cholesteryl ester of oleic acid in liquid paraffin by rubbing glass on glass increases the load capacity by six to seven times compared to a medium containing oleic acid. At the same time, the SEM method and profilometry at loads of more than 4 MPa established the formation of microgrooves on the rubbing surfaces (Fig. 4), which do not affect the friction characteristics.

Optically active substances were detected in the microgrooves by the method of polarizing microscopy (Fig. 5). According to [8, 10], such a surface relief determines the groove-oriented arrangement of molecules of liquid-crystalline cholesterol compounds. In this case, the cholesteric and nematic liquid crystals form a planar texture. The cohesion energy of molecules of liquid crystal compounds in this case can be significant. In particular, it is well known that in the case of strong adhesion to reorient the molecule of cholesterol compounds across the groove of the microrelief, requires an electric field of more than 1×10^6 V/cm.

This property for the studied cholesteryl ester of oleic acid as the typical representative of liquid crystalline compounds of cholesterol, apparently, determines the high bearing capacity of its boundary lubricating layers formed on the friction surfaces by structurally ordered molecules of cholesteryl ester of oleic acid.

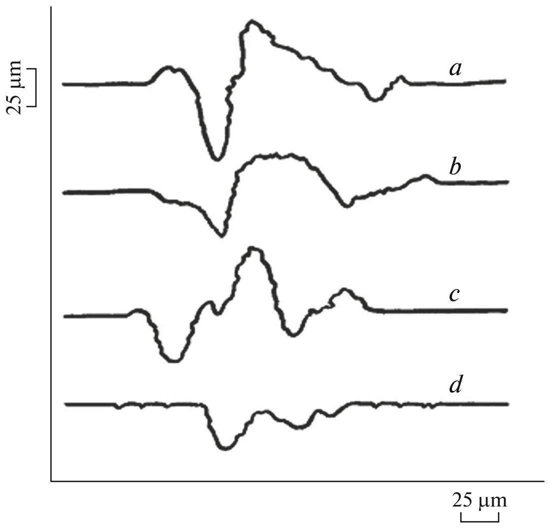

Fig. 3. Profilograms of the surfaces of glass samples after friction: (*a*) without lubrication; (*b*) when lubricated with vaseline oil; (*c*) with the addition of 3 wt % oleic acid; (*d*) with the addition of 3 wt % of holo-sterile oleic acid ether; (*a*, *b*, *c*) p = 1.2 MPa; (*d*) p = 7.0 MPa; V = 0.1 m/s.

This is confirmed not only by an increase in the load capacity but also by the nature of the destruction of the rubbing surfaces. Thus, in the case of a lubricating medium with the addition of liquid-crystalline cholesterol compounds, destruction was observed only in certain areas of the contact of rubbing glasses at loads of more than 7 MPa (Fig. 2d). At the same time, in the case of media that did not contain cholesteryl ester of oleic acid, the friction surfaces of the glasses began to set at loads that were lower by factors of 6 to 7 (Figs 2a–2c).

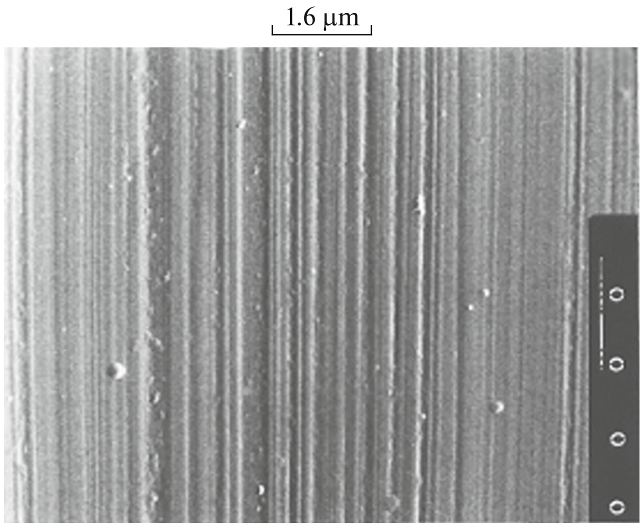

Fig. 4. The surface of the glass sample after friction at p = 6.0 MPa and V = 0.1 m/s in vaseline oil with the addition of 3 wt % of oleic acid of cholesterol ester.

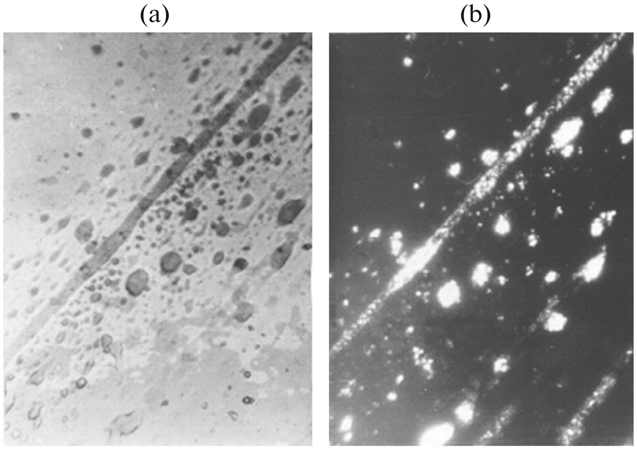

Fig. 5. The area of friction on the surface of glass samples: (a) in unpolarized light; (b) in polarized light (×435).

In this case, in the IR spectrum of oleic acid after friction, a sharp decrease is found in the intensity of the absorption band in the region of 3012 cm^{-1}, corresponding to the stretching vibrations of the CH groups near the double bonds and the appearance of absorption bands in the regions of 970 and 1740 cm^{-1}, which are a high-frequency shoulder to the absorption bands in the regions of 950 to 1712 cm^{-1}, respectively. The appearance of a doublet of 950 and 970 cm^{-1} in the spectra of higher fatty acids is related to the change in the energy of the hydrogen bonds of dimerized acid molecules. These changes give reason to believe that in the process of friction, the double bonds in the hydrocarbon radical of oleic acid open with the formation of high molecular weight compounds. The latter contributes to their destruction with the formation of active products with a dispersing effect that intensify the process of wear of the friction surfaces. Meanwhile, when chemically inactive surfaces are lubricated with cholesteryl ester of oleic acid, no mechanochemical processes are observed, as indicated by both the absence of changes in the IR spectra recorded before and after the experiment in this liquid crystal medium and the stability of the friction regime throughout the test. (Fig. 1, curve *3*).

CONCLUSIONS

The results of the studies show that the addition of liquid crystal cholesterol compounds to the lubricant for chemically inactive surfaces is very effective, because they allow significantly increasing the load capacity of the friction pair.

FUNDING

The research was carried out with the financial support of the Belarusian Republican Foundation for Fundamental Research (project no. T20R-019) and the Russian Foundation for Basic Research (project no. 20-58-00004).

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