

Study of the Mechanism of the Transformation and Transfer of Contact Layers in the Lubricating Medium–Surface Tribopair System

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Abstract—With the purpose of improving the method for the in-place-repair of the surfaces of machinery parts and reducing friction and wear parameters due to the action of a reductive lubricating composition (RLC), the mechanism of the transformation and transfer of contact layers in the bulk of the lubricating medium between the RLC components and the reconstructed surface is studied. A hypothesis of how the contact layers of the lubricating medium are transformed and transferred and are consecutively subjected to deformation, shear, and removal into the bulk, being then replaced by new contact layers of lubricating medium, is put forward. A theoretical analysis shows that the most important factors for increasing the efficiency of RLC are the structuring of the lubricating medium by nanosized metallic elements and the selective aggregation and removal of wear products and oil oxidation products on a filter. These conditions are provided by increasing the effectiveness of the traditional RLC and other additives and by introducing into the lubricating medium a mixture of nitrogen-containing components, such as ammonium hydroxide and urea. Adding the modified oil composition into commercial oil makes it possible to double its repair-recovery and antiwear capabilities. The additives proposed are effective at low dosages (3 vol % in oil), being, in addition, nontoxic and posing no hazard when handled and transported.

Keywords: in-place-repair, repair-recovery lubricant composition, friction, wear, shear, deformation, compensation layer, ammonium hydroxide, urea

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The main problem of modern tribology is to reduce the wear and tear of machinery, i.e., increase its service life, while enhancing the intensity of its operation. To restore the surfaces of machine parts, reduce friction and wear, a new direction has emerged in the last decade, associated with in-place repair based on the action of reductive lubricating composition (RLC). A positive effect of the RLC components in the simulated medium is achieved when the composition of the compensation layers corresponds to the composition of the medium (Fig. 1b), while the state of the medium favorably changes in accordance with the role of the components of the reducing lubricant composition [1, 2].

The active components of RLC are metal elements, which are kept in static conditions in the lubricating medium by compensation layers (Fig. 1). Under static conditions, each solid-phase component is compen-

sated by at least two layers (Fig. 1a) of different natures [1–3]. In these conditions, the RLC elements are subject to a constant all-round compression [1],

$$P_x = P_y = P_z = \text{const}, \quad (1)$$

under which the specific orthogonal hydrostatic stress for the i th component of the RLC is determined by the ratio of the pressure P_i to the surface area of the component S_i [3]:

$$\sigma_i = \frac{P_i}{S_i}. \quad (2)$$

According to (1), the hydrostatic stress along all axes is also constant:

$$\sigma_x = \sigma_y = \sigma_z = \text{const}. \quad (3)$$

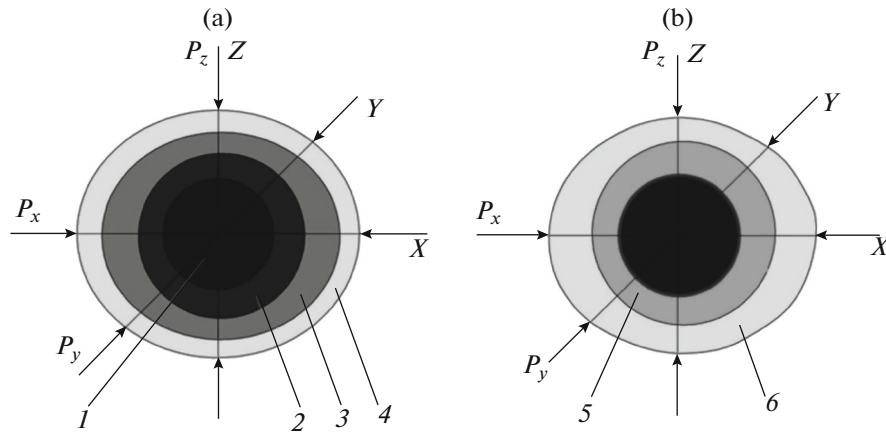


Fig. 1. Scheme of near-surface RLC layers: (a) (1) metallic RLC element, (2, 3) compensation layers of the intermediate medium, (4) modified medium; (b) (5, 6) compensation layers corresponding to the modified medium composition.

This state can be represented by the average hydrostatic stress [1, 3]:

$$\sigma_n = \frac{\sigma_x + \sigma_y + \sigma_z}{3}. \quad (4)$$

A state characterized by the equality of the normal stresses along the accepted axes is known as the volumetric stress state. The full characteristic of the stress state includes additionally an expression for tangential stresses τ_i , acquiring maximum values in directions at an angle of 45° between the principal normal stresses, defined as

$$\tau_i = \tau_{\max} = \frac{\sigma_{\max} - \sigma_{\min}}{2} > 0, \quad (5)$$

where σ_{\max} and σ_{\min} are the maximum and minimum stresses.

Under static conditions, because of the opposite signs and large values of $\sigma_{\text{det}} - \sigma_x = -\sigma_y = -\sigma_z \ll +\sigma_{\text{det}}$ [1, 3], practically no intermolecular separation in the “RLC components–compensation layers” chain takes place. The component of the oil medium objects on the basis of compensation contact layers is very small, so the layers do not mix with the bulk of the medium, and the modification and restoration of the interfaced parts is impeded [1, 4]. For their effective recovery, it is necessary to ensure conditions providing for the inequality of the pressures or normal stresses along the X , Y , and Z axes [1, 2],

$$P_x \neq P_y \neq P_z, \quad \sigma_x \neq \sigma_y \neq \sigma_z, \quad (6)$$

and for the maximum possible tangential stresses (τ_{\max}),

$$[\sigma_x > \sigma_y > \sigma_z] \sim [\sigma_1 > \sigma_2 > \sigma_3], \quad (7)$$

defined as:

$$\tau_{\max} = \frac{\sigma_1 - \sigma_3}{2} \gg 0. \quad (8)$$

Under the condition

$$\tau_{\max} \geq \tau_{\text{shear}}, \quad (9)$$

the contact is deformed, which is necessary that it was displaced into the bulk of the medium [1, 5]. The proposed hypothesis of transformation of the transfer of contact layers, their sequential deformation, displacement and removal into the bulk with replacement by new contact layers of the lubricating medium is illustrated in Figs. 2–4. This means that the creation of gradients of stressed states and stress rates around the RLC elements can occur due to cavitation and thermal motion during the operation of the lubrication pump or centrifuge [1, 5, 6]. The mechanisms of transfer of structural states into the bulk and of formation of objects from compensation layers and a scheme for volumetric compensation of RLC by objects built of oil molecules are shown in Fig. 4, respectively. At a certain magnitude of tangential stresses, the ion-compensation layer separates to form objects with nuclei based on this layer. Since the bonds of these nuclei with the outer layers represent intermolecular interactions, they are easily broken due to the cavitation caused by thermal motion during the operation of the lubrication pump or centrifuge [2, 5]. A further deformation of the compensation layers will be associated with the formation of a plane stressed state, so far as the following inequalities is satisfied:

$$P_x = P_y \ll P_z, \quad \sigma_x = \sigma_y \ll \sigma_z. \quad (10)$$

Thus, the magnitude of the tangential stresses is determined by the level $\sigma_x = \sigma_y$ with respect to σ_z or the difference $\sigma_2 = \sigma_3 - \sigma_1$. At the same time, the level $\sigma_2 = \sigma_3$ is determined by the resistance of the medium in the XY plane. The magnitude of the resistance depends on the rate of application of the load V along the Z axis [7]. In addition, the implementation of an effective process of modifying and restoring the parts also depends on the material of the component

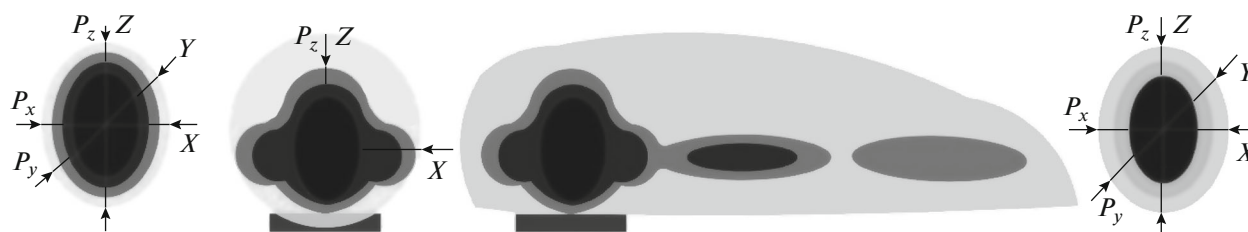


Fig. 2. Stages of replacement of the impurity contact layer by a lubricating medium layer.

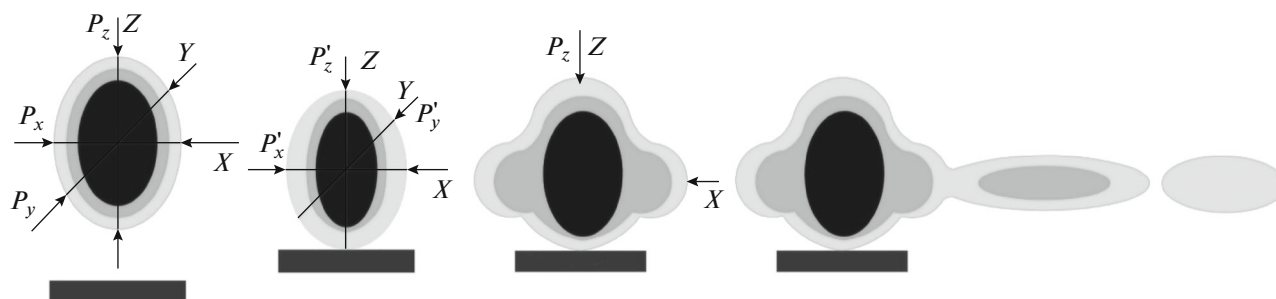


Fig. 3. Transfer of the structural components of the contact layer into the bulk of the lubricating medium.

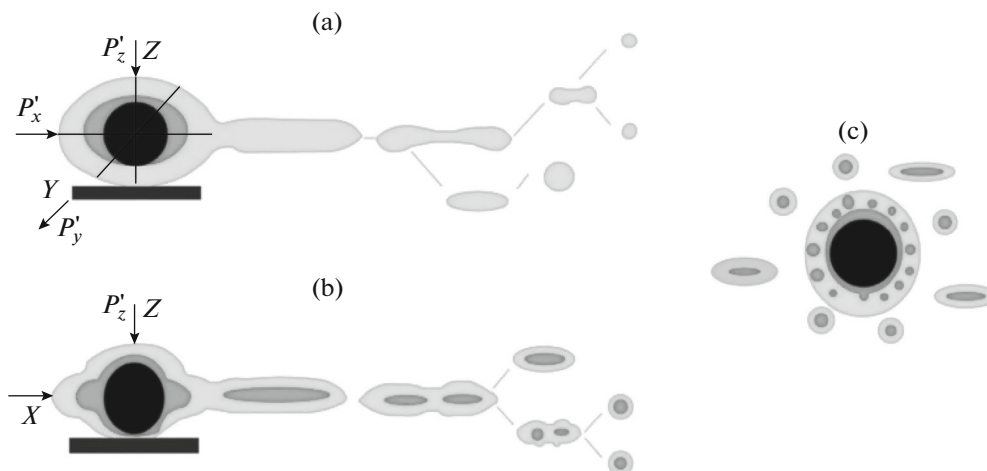


Fig. 4. Formation of objects under the influence of RLC and dynamic processes in the oil: (a) mechanism of the transfer of structural states into the bulk of the lubricating medium and formation of objects on the basis of the first compensation layer; (b) the mechanism of the transfer of structural states into the bulk and the formation of objects on the basis of the second compensation layer; (c) scheme of volumetric compensation of RCL by objects comprised of oil molecules.

introduced, temperature, and other conditions [8]. For example, all other conditions being equal, with increasing temperature, the deformation and shift of the compensation layers in intramolecular volumes manifest themselves to a greater extent [9]. The magnitude of the shear resistance of the near-surface layer for the intramolecular and intermolecular volumes is also different [10, 11].

Higher shear strengths are manifested in the layers with ultradispersed and nanodispersed components τ_{nc} and then in the ion-forming τ_{ifl} and ion-compen-

sating τ_{icl} layers. The subsequent layers are known to belong to the region with easy slip, with τ_{esl} for them being several orders of magnitude smaller:

$$\tau_{nc} > \tau_{ifl} > \tau_{icl} \gg \tau_{esl}. \quad (11)$$

However, despite a relatively low resistance to shear for the first three components, the plane stress state of deformation in these layers may not be realized because of the relaxing effect of successive layers. A stable deformation can be achieved by changing the properties of the lubricating medium or by providing,

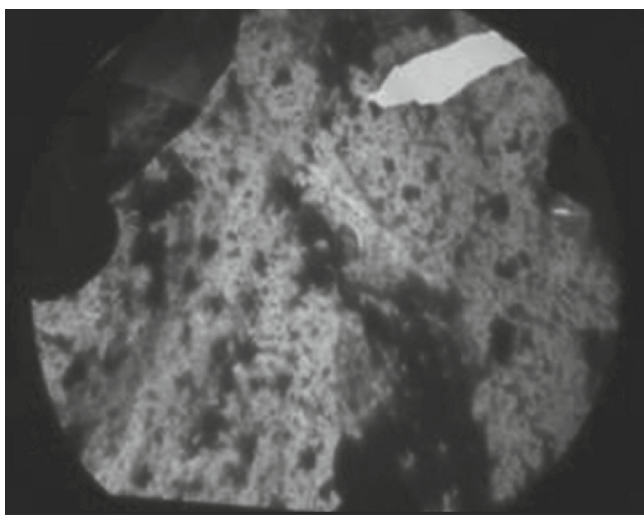


Fig. 5. Microphotograph of a film of initial lubricating composition ($K_{\text{mag}} = 220000\times$).



Fig. 6. Microphotograph of a film of modified lubricating composition ($K_{\text{mag}} = 220000\times$).

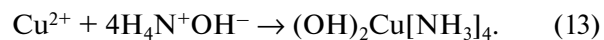
in other ways, a comparable stress state in the bulk and in the easy-slip layers. In this case, the maximum tangential stresses in the easy-slip layers should be lower than the corresponding shear resistances:

$$\tau_{\text{max(esl)}} < \tau_{\text{esl}} \quad (12)$$

If a plane stress state arises, the tangential stress increase significantly. Conditions are created for the simultaneous separation of the ion-formation and ion-compensation layers with the formation from these layers of objects comprised of oil molecules with a core built based on the first compensation layer. Because of formation of such objects, the thickness of

the ion-forming layer decreases, but the compensation of the surface imbalance of the object is not violated, since the separated layers and the objects formed from them are removed to distances not exceeding short-range values. Thus, the compensation of the surface of the RLC particles is supplemented by the bulk compensation of the already formed objects of the medium. Despite this, the oil-built objects remain predominantly in the field of action of RLC particles and their uniform distribution in the bulk remains difficult to achieve. For the oil objects to be uniformly distributed in the bulk, they should be structured by assembling into so-called “superlattices” (SL). In this case, it is easier to produce a deformation of the contact layer, which, in turn, provides the necessary conditions ($\tau_{\text{max(esl)}} < \tau_{\text{esl}}$) for its displacement into the bulk of the medium [1, 7].

We propose here a method for creating superlattices from highly disperse RLC particles (brass, copper, or molybdenum disulfide). It was found that the introduction of ammonium hydroxide (H_4NOH) into the RLC promotes a further grinding of the RLC elements to a highly dispersed powder with particle size of $d < 1 \mu\text{m}$ and a uniform distribution throughout the oil medium. The disperse composition was optimized by successively increasing the concentration of ammonium hydroxide in the RLC at a temperature of 25°C . The mixture was stirred for 15 min and analyzed under an electron microscope with a magnification of $220000\times$. Figures 5 and 6 show that, as the H_4NOH concentration increases, the size of the RLC particles decreases. At the same time, the mobility of the composition decreases, and eventually, 10% H_4NOH , it transforms into to a non-mobile gel, probably due to the reaction of ammonium hydroxide with the oxide films of the RLC metallic components. This is confirmed by a decrease in the intensity of the bands of the OH group of ammonium hydroxide in luminescent and IR spectra and by the formation of a blue precipitate characteristic of copper ammonia:



The efficiency of structuring of RLC with ammonium hydroxide was evaluated by comparing the weight of the precipitates formed during centrifugation of oil samples containing 3% standard RLC and oil samples containing 3% of modified (RLC_M) composition (RLC + 10% H_4NOH). The oil used in the experiment was characterized by the following parameters: the alkaline number, 3.5 mg KOH/g; acid number, 1.6 mg KOH/g; kinematic viscosity, 9.8 mm²/s; and content of precipitate insoluble in isoctane, 0.09%. The oil samples were centrifuged at a speed $n = 3000 \text{ rpm}$ for 15 min and filtered; the filter cake was washed with ether, dried at 60°C to constant weight, and weighed. The weight of the precipitate in the test tube containing RLC turned out to be 20 times that in the test tube containing RLC_M. The results listed in Table 1 show

that most of the active elements of RLC_M remain in the running oil. Similar results were observed for $t = 80^\circ\text{C}$ and $n = 4000$ rpm, conditions close to those typical of ICE operation. The data obtained indicate a high emulsion stability of the modified composition in the oil. This makes it possible, by preventing the deposition of RLC_M elements on the oil filter and the channels of the ICE lubrication system, to maintain the optimum concentration of RLC_M in the oil, increase the efficiency of in-place-repair, and improve the tribotechnical characteristics of the lubricating medium.

At the same time, oil oxidation products accumulate during engine operation. As a result, conditions arise under which RLC, as well as detergent-dispersant, antioxidant, antiwear, and other additives, normally present in oils, gradually lose their effectiveness. Therefore, in the present work, we performed studies aimed at decreasing the content of oil oxidation products. The object was an oil containing a RLC additive in the form of a 0.2–60- μm -particle mixture of molybdenum disulfide (Mo–S–S–Mo) with a 2 : 1 brass–phosphorus alloy. The ratio of the RLC components in M10G2k mineral oil was 55 : 30 : 15. Microscopic examination at a magnification of $140\times$ showed that, when introduced into fresh motor oil, retained its dispersion composition and particle size. However, when RLC was introduced into a motor oil containing oxidation and wear products, the particles aggregated, not only coarse-grained ($d \geq 20\text{--}100\ \mu\text{m}$) but also finely dispersed ($d \geq 1\text{--}10\ \mu\text{m}$) RLC, being deposited on the walls during centrifugation. Thus, experimental studies have confirmed the theoretical prediction that the efficiency of in-place-repair is closely related to the degree of nanodispersed structuring of RLC elements. To effectively use the in-place-repair technology, it is necessary to use RLC_M in the form of a highly dispersed powder with particle size $d < 1\ \mu\text{m}$.

The concentration of oxidation products was reduced by means of coagulation with nonionic flocculants and subsequent removal on the oil filter. The flocculant was urea dissolved in 25% ammonium hydroxide, which was selected according to the criteria of efficiency, cost, and environmental safety. The changes in the dispersion composition and the rearrangement of the metallic RLC elements caused by the

Table 1. Precipitate weight after centrifugation of the modified oil samples, ($V = 4\ \text{mL}$)

Type of oil	Precipitate weight, g
M10G2k + RLC	0.001
M10G2k + RLC_M	0.02

flocculant were monitored using an EMB-100A electron microscope. Accurate measurements of the dispersion composition of the oil oxidation products were carried out on a “Digital Microscope” instrument. The concentration of urea and the temperature of the oil at which the enlargement of the impurities is optimal for their subsequent removal on an OPn-8UKhL42 laboratory centrifuge. To assess the degree of removal of impurities, microphotographs of the oil sample before and after each experiment were taken [12].

At a 0.1% concentration of urea in the running motor oil, a weakly pronounced process of coagulation of the oxidation products was observed (Fig. 7b). However, at an urea concentration of 0.3%, the coarsening of resin and asphaltene particles from 1 to 20–50 μm occurs rapidly (Fig. 7c). A further increase in the urea concentration produced no significant changes in the dispersion composition of the impurities. As follows from Fig. 8, the aggregation of impurities in the presence of 0.3% urea in the running motor oil proceeds most effectively at temperatures between 70 and 100°C. The nature of the change in the appearance of the oil after 100-h operation, oil after introduction of RLC_M , and oil after subsequent centrifugation are shown in Figs. 9a–9c, respectively. As can be seen, the presence of urea has a positive effect on the chemical reduction of oil oxidation products. According to a spectral analysis of oils with urea additives, the content of oxides decreased by 0.3–0.5 rel. units, approaching the indicators for fresh motor oil.

As is known [13, 14], the interfaced surfaces of the internal combustion engine often operate under boundary lubrication conditions. In extreme conditions, the reason for the destruction of boundary lubricant layers, which damages these surfaces, is a sharp increase in the temperature in the frictional contact to 150–250°C. Modeling these conditions on a

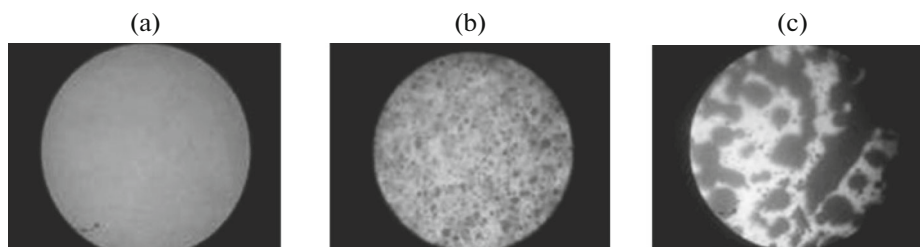


Fig. 7. Characteristics of the process of enlargement of motor oil oxidation products: (a) initial oil, (b) oil seeded with 0.1% urea, (c) oil seeded with 0.3% urea.

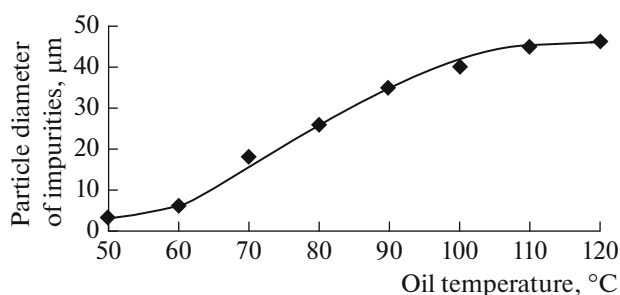


Fig. 8. Dependence of the coagulation ability of the particles on the oil temperature.

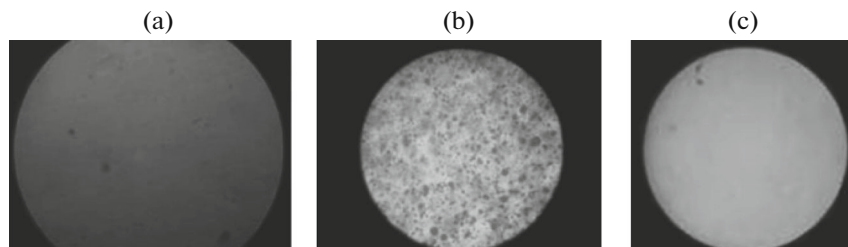


Fig. 9. Microphotographs of samples of tested oils: (a) M10G2k motor oil after 100 h of operation, (b) M10G2k after introduction of the lubricating composition, (c) M10G2k after removal of impurities by centrifugation ($T_M = (80 \pm 5)^\circ\text{C}$, $n = 4000$ rpm, $t = 25$ min).

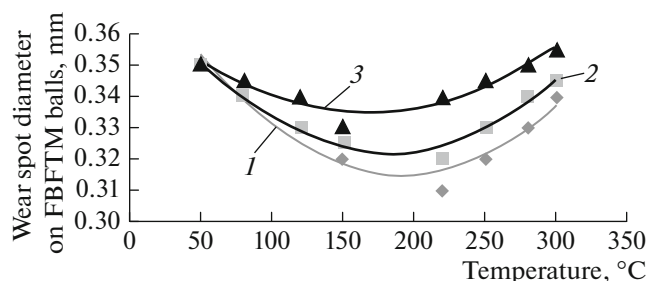


Fig. 10. Dependence of the change in the diameter of the wear spots on the balls of the four-ball friction test machine on the oil temperature: (1) M10G2k oil + 3% RLC_M , (2) M10G2k oil + 3% RLC, and (3) M10G2k oil.

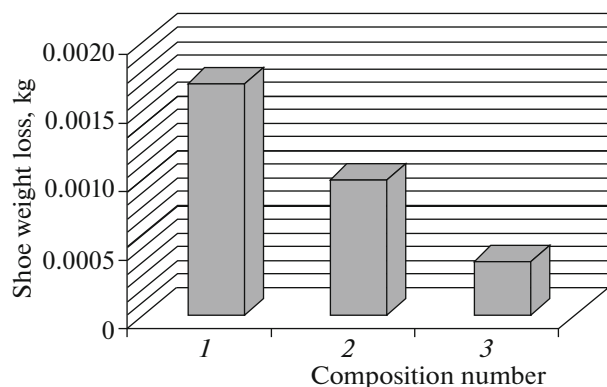


Fig. 11. The degree of wear, estimated by the loss of weight of shoes: (1) M10G2k oil, (2) M10G2k oil + 3% $\text{RLC}_{\text{Cluster}}$, and (3) M10G2k + 3% RLC_M .

four-ball friction test machine showed that the anti-wear properties of M10G2k + RLC_M modified oil, characterized by a decrease in the wear spot diameter, improved almost twofold in comparison with M10G2k commercial oil (Fig. 10). The results on the weight loss of shoes on a friction test machine are displayed in Fig. 11. As can be seen, the loss of the weight of the shoes during tests of oils with RLC_M is two times lower than that for oils containing unmodified RLC. In terms of the coefficient of friction under load (N/m^2), the developed lubricant also significantly exceeds both M10G2k commercial oil and oil with standard RLC additive. For example, after 20 min of testing on shoe no. 1, which operated in M10G2k oil, the load had to be reduced to $P = 7 \text{ N}/\text{m}^2$ to avoid the jamming of the friction test machine. For shoe no. 2, in which case M10G2k oil with RLC additive was used, the load was reduced after 120 min. By contrast, for shoe no. 3, which operated in oil with RLC_M , it was not necessary to reduce the load. The efficiency of the improved composition is clearly demonstrated by the wear pattern of the shoes shown in Fig. 12.

Thus, the theoretical predictions of the promising prospects of structuring the RLC and lubricating medium were confirmed experimentally. Structuring the RLC with ammonium hydroxide makes it possible to improve its recovery and tribotechnical characteristics, which enhances the efficiency of in-place-repairs. The introduction of urea into the oil contributes to the agglomeration of the oil oxidation products, thereby facilitating their removal, and to the restoration and prolongation of the service life of the

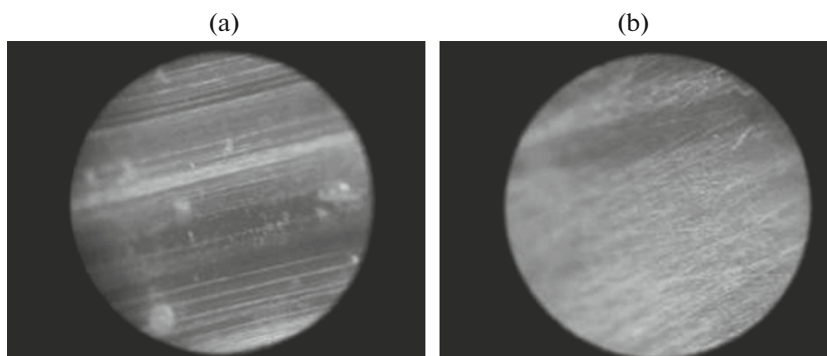


Fig. 12. Microphotographs of the friction surfaces of the shoes: (a) M10G2k oil and (b) M10G2k oil + RLC_M .

motor oil [15–18], which solves the problems of resource conservation.

REFERENCES

1. V. V. Ostrikov, V. P. Shelokhovostov, and S. Yu. Popov, in *Proceedings of the 8th International Conference on Demand from the World of Science 2012* (ByalGRAD-BG, Sofia, 2012), Vol. 38, p. 13.
2. V. S. Grigor'ev, A. V. Roshchin, S. S. Khokhlov, A. F. Eleev, K. N. Gerasimov, Yu. A. Mazalov, A. V. Dunaev, and V. V. Ostrikov, *Russ. J. Phys. Chem. B* **9**, 461 (2015).
3. V. V. Ostrikov, V. P. Shelokhovostov, and S. Yu. Popov, in *Proceedings of the 8th International Conference on Dynamics of Scientific Researches 2012* (Nauka i studia, Przemysl, 2012), p. 32.
4. V. V. Ostrikov, A. G. Zimin, and S. Yu. Popov, *Nauka Tsentr. Ross.*, No. 5, 30 (2013).
5. V. M. Agranovich and D. L. Mills, *Surface Polaritons. Electromagnetic Waves at Surfaces and Interfaces* (Nauka, Moscow, 1985; North-Holland, Amsterdam, 1982).
6. V. P. Shelokhovostov and V. N. Chernyshov, *Methods and Systems of Diagnostics Nanomodified Condensed Media* (Spektr, Moscow, 2013) [in Russian].
7. *Additives for Oils, Proceedings of the 2nd All-Union Workshop*, Eds. by S. E. Krein and P. I. Sanin (Khimiya, Moscow, 1966).
8. *Physics of Liquid Crystals*, Ed. by A. S. Sonin (Mir, Moscow, 1977) [in Russian].
9. A. V. Panin, Doctoral (Phys. Math.) Dissertation (Tomsk, 2006).
10. A. S. Prizhimov, Cand. Sci. (Phys. Math.) Dissertation (Voronezh, 2006).
11. V. Ya. Dimikhovskii and G. A. Vugal'ter, *Physics of Quantum Low-Dimensional Structures* (Logos, Moscow, 2000) [in Russian].
12. V. V. Ostrikov, S. Yu. Popov, and A. G. Zimin, *Nauka Tsentr. Ross.*, No. 2, 42 (2014).
13. M. Khebda, *Handbook of Tribotechnics. Theoretical Principles* (Mashinostroenie, Moscow, 1989), Vols. 1, 2 [in Russian].
14. V. I. Balabanov, *Met. Sci. Heat Treatm.* **43**, 288 (2001). doi 10.1023/A:1012737606014
15. V. V. Ostrikov and S. N. Sazonov, *Sel'sk. Mekhanizator*, No. 10, 32 (2012).
16. V. V. Ostrikov, S. N. Sazonov, and D. D. Sazonova, *Agroprom. Kompleks Ross.*, No. 68, 76 (2014).
17. V. V. Safonov, A. S. Azarov, and A. L. Kukushkin, *Nauch. Mysl'*, No. 3, 34 (2015).
18. V. V. Ostrikov, A. G. Zimin, S. Yu. Popov, and V. V. Safonov, *Dvigatelistroen.*, No. 2, 32 (2014).

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