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STRENGTHENING OF FRICTION SURFACES BY USING GEOMODIFIERS BASED ON SERPENTINES FROM THE DASHUKIVKA DEPOSIT

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The object of research is the process of improving the tribological characteristics of friction joints, in particular anti-wear and anti-burr properties.

There is a practice of using serpentines, so-called "friction geomodifiers" (FGM), as special repair and restoration additives. Their use leads to a decrease in the coefficient of friction and temperatures in the contact zone; an increase in the mass of parts is observed, which indicates the restoration of worn surfaces. The mechanism of formation of new structures is still unclear. There are hypotheses that severe friction conditions initiate micrometallurgical processes at the atomic-crystalline level, as a result of which modified layers with unique tribological characteristics are formed on the surfaces.

A comparative analysis of the main indicators of serpentines of the Dashukivka deposit in terms of chemical composition and structure showed their correspondence to widely known analogs but they were never used in such a capacity.

According to the results of the tests, the additives have shown their effectiveness as geomodifiers of friction. Addition of 4 % serpentine to the lubricating composition based on I-20 A oil reduced the wear rate by 2–3 times, the friction moment by 15 %, compared to I-20 A without additives.

An increase in surface microhardness was observed, from 6 GPa for the basic variant to 10 GPa, for the variant with FGM additives.

It has been established that the use is most effective for heavily loaded friction pairs (ship fittings, hatch closures, etc.) as it increases the clamping load (from 600 to 1400 N for a pair of steel 45/ShKh15); with increasing load, the coefficient of friction and the rate of wear decrease.

The results confirm the need to expand research into this area to solve the complex problem of increasing the reliability of tribojunctions

Keywords: repair and restoration technologies, friction geomodifiers, serpentine, heavily loaded friction pairs

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1. Introduction

Malfunction, or failure of heavily loaded mechanisms, is mostly associated with the processes of jamming, non-rotation, seizure – i.e., wear and tear in the friction nodes with which they are equipped. And the wear resistance of such nodes is most often associated with the peculiarities of the course of friction processes and the nature of the wear of the surface layers in the contact zone. Most ship's deck machinery is equipped with such mechanisms (hatch closures, appliances, etc.), which, according to the regulations of use, must withstand significant loads at low rotation speeds and have a long period between repairs. The increase in the number and nomenclature of such mechanisms makes it necessary to thoroughly investigate the tribological properties of friction surfaces and to propose the latest technological approaches to increase their durability based on modern theoretical knowledge.

There are proven methods of increasing wear resistance and reliability of friction units at the design and technological stages. Various methods of modifying the properties of the surface layer (thermal, chemical-thermal treatment, differential strengthening, strengthening by surface-plastic deformation, micro-profiling, coating, and many others), methods of optimizing the design of friction nodes are considered promising [1–4]. But in order to increase the reliability of working mechanisms on ships in operation, it is advisable to offer technologies of indiscriminate intervention in the friction zone, which can be done by introducing original lubricating materials with a special influence on the course of tribological processes.

The development of new lubricating materials is a promising area of tribology. This applies to both basic materials and various additions, fillers, additives. They can improve the properties of lubricating compositions, expand the areas of their application (structures of nodes, operating conditions, temperatures, loads, speed, peculiarities of environments) [5].

The field of "geotribology" studies the regularities of the processes of friction, wear and lubrication under the conditions of the use of various kinds of minerals and other compounds of geological origin. Such materials, mainly based on crushed and modified serpentine, as well as other minerals of natural and artificial origin, were named geomodifiers or geoactivators.

Friction modifiers are additives and impurities that reduce the coefficient of friction between friction surfaces, reduce their wear and destruction. Natural minerals of the serpentine class, called "friction geomodifiers" (FGM), are also used as special repair and restoration additives. Geomodifiers do not change the properties of the lubricant and affect only metal friction surfaces, increase their microhardness, and optimize roughness. The serpentines of the Dashukivka deposit (Ukraine) are similar in chemical composition and structure to well-known analogs, but they have never been used in such a capacity.

Wear processes are difficult to predict and practically impossible to observe under real operating conditions when the operating factors change. Therefore, separate experimental studies of FGM from serpentines of the Dashukivka deposit and their theoretical description are scientifically justified. In practical application, it can even be about self-healing of worn surfaces.

Another reason for the insufficient use of the unique properties of geomodifiers is the high cost of the obtained preparations, although many of them have reached the stage of industrial production.

Thus, research into the use of geomodifiers for the benefit of tribology, in particular on the basis of inexpensive bentonites, can be considered relevant.

2. Literature review and problem statement

Studies [6] showed that additives based on serpentines can form a self-healing film, which significantly reduces the degree of wear of friction pairs. The main elemental composition of the film is Fe, O, Si, C, and Mg, which indicates that the additives are directly involved in the formation of the self-healing film. It was shown in [7] that the recovery effect is due to the formation of a two-level structure on the friction surfaces. This structure is a mineral skeleton with a developed surface and a layer formed by tribopolymerization products of the lubricant. The authors of [8] obtained results regarding the interaction of powdery laminar hydro silicates of the serpentinite type with friction surfaces. The formation of protective layers of metal-ceramics caused by the atomic-molecular structure of layered hydro silicates was observed. The results of observations [9] showed that in the process of friction and wear, serpentine particles that enter into physical or chemical reactions with the surface of the studied samples create a layer of protective film. Thus, this type of admixture has the function of filling the furrow of the surface of the friction pair, which reduces the surface roughness, the degree of friction and wear.

In the cited works, the principle mechanism of the processes in general, by which well-known FGMs work, is described. For the Dashukivka serpentines, it is necessary to investigate to what extent they correspond to such a tribological picture.

Research [10] reports the results of experimental friction tests in the presence of serpentine additives in the lubricant. The replacement of magnesium atoms of the mineral structure by iron atoms from the friction surface was observed. As a result, there is a recombination of the crystal lattice and the formation of pseudo mineral structures similar to SiO. Studies [11] of an improved additive based on silicates showed that a smooth outer layer with a high carbon content was formed on the surface of the sample, which indicates the possible formation of diamond-like carbon films. Ferrographic analysis showed that "negative wear" occurred during the introduction of the additive, i.e., self-healing of the surfaces. The materials of the listed works direct the authors to choose those research methods the results of which will become convincing scientific evidence arguments in favor of serpentines and will be included in the general scientific theory of the process.

Since the working mechanisms of geomodifiers are at the stage of scientific discourse, it is necessary to direct research according to one of the common hypotheses, among which the following are distinguished in [12]:

– creation of protective structures as a result of the pressing of serpentine particles on the friction surface; the main factor in the formation of a protective structure (coating) is mechanical pressure;

– the formation of a protective layer as a result of micrometallurgical processes with the diffusion of components of the triboenvironment into the surface layer; the main active factors are high temperature and pressure in the friction zone;

– the hypothesis of two-stage mechanothermal destruction of serpentine particles, which is accompanied by reactions of replacement of magnesium atoms by iron in the serpentine, adhesion of new components and possible diffusion of magnesium;

– creation of iron-magnesium glass, which has a high affinity for iron; this explains the high physical and mechanical indicators of the new layers (hardness, smoothness, electrical resistance, heat resistance, and transparency). But the hypothesis does not explain the oiliness of the film and the presence of a large amount of carbon in the structure;

– the hypothesis of a specific, rarely realizable selective transfer;

– a hypothesis that takes into account the auxiliary process of varnish formation due to the thermal destruction of oils and the deposition of heavy fractions in the form of films; the authors of research on RBC processes show that the presence of oil is not a necessary condition for the formation of coatings, although there are no protocols for such tests;

– the hypothesis of the sequence of various processes [13]: in the friction process, the serpentine particles are crushed to optimal sizes (up to 2 μm), the friction surfaces are polished, freeing them from oxide films and defective weakened structures, and are pressed into the depressions of the microrelief. Due to the released heat in the presence of the catalyst (including the juvenile surface of the metal), ion-exchange reactions are accelerated, magnesium atoms are replaced by iron atoms, and iron atoms are replaced by magnesium. Then, under the influence of high temperatures and pressures, particles are sintered, and a protective anti-friction layer is formed. The rate of layer formation is proportional to the pressure and temperature in the area of the actual area of contact.

Each of the hypotheses has conditions or limitations.

The hypothesis of non-silicate layers [14] is that silicate particles do not take part in the formation of a reduced layer but act only as a catalyst that initiates a number of complex tribochemical reactions under conditions of high temperatures and pressures. As a result, a regenerated layer with an amorphous carbon structure is formed on the worn surface. However, the proportional amount of silicates used as process catalysts and how many are transformed into an amorphous structure has not been determined. In the case of inconsistency, an abrasive process may occur.

Works [15, 16] formulated a hypothesis of the formation mechanism of modified layers of serpentine nanopowders activated by high temperature in the friction zone. But the formation of a high-temperature zone is assumed under conditions of high-speed friction, which is not typical for heavily loaded nodes.

Study [17] showed that the addition of serpentine powder to engine oil (5 mg/ml with a particle diameter of up to 2 μm) led to the restoration of worn surfaces of diesel locomotives. The hardness of the newly formed surfaces is twice that of the base material, the surface roughness $Ra \approx 0.0694$ μm, the coefficient of friction between the piston ring and the cylinder mirror $f=0.005$. In known scientific studies [18], a constant decrease in the coefficient of friction was observed under loads in the range of 10–100 N when adding 0.5 wt% of ultradispersed magnesium aluminosilicate powders. Data in [17, 18] highlight the results of FGM operation in units with oil filters, where partial losses of nanopowders are possible. And Dashukivka serpentines are offered for lubricating mixtures in filter-free closed systems; the quantitative values of additives require experimental and analytical calculations.

In work [19], the tribological characteristics and restorative effect of the mixture with the addition of 5 % hydroxymagnesium silicate on the friction of steel pairs with different surface roughness were investigated. It was shown that there is a relationship between the regenerating effect and the average size of silicate particles – the most positive effect was observed when the average diameter of the particles coincided with the roughness of the friction surface. But the addition of FGM is carried out by an indiscriminate method to the worn friction pair, when it is impossible to determine the existing roughness, and it is necessary to apply a powder with an extended dispersion range. Such conditions are not considered in the work.

In [20], it is shown that on a worn surface using 1.5 % of the mass fraction of serpentine dispersed in the base mineral oil, a nanocrystalline tribofilm with a thickness of 500–600 nm is formed, which consists of Fe_3O_4, FeSi, SiO_2, AlFe, and Fe–C (Fe_3C) compounds. The compounds that are formed are very effective and necessary from the friction zone, but the process of their guaranteed formation from the Dashukivka serpentines is completely unexplored.

Based on research materials [21], it was established that the film-forming ability of ultradispersed serpentine powders increases in the temperature range from 300 °C to 600 °C. At a temperature above 850 °C, the structure of the layer is destroyed, wear and the coefficient of friction increase. The reasonable limit temperature conditions presented in the paper should be extrapolated to heavily loaded friction units in marine engines. Such a problem has not been solved today, and it requires research.

Summarizing the known results of scientific research based on the review of literary sources, one should note the predominantly positive effect of serpentine impurities on the reliability of friction joints. And based on the fact that the serpentines of the Dashukivka deposit are similar in chemical composition and structure to well-known analogs (France, Hungary, etc.), there are grounds for creating effective lubricant additives from them. Such additives could, as a result of interaction with the friction areas of the parts, form a metal-ceramic layer on them and, as a result, restore the friction surfaces. The prospect of using Dashukivka serpentines is also attractive in terms of their value – they are much cheaper than their counterparts.

All this gives reason to assert that it is expedient to carry out research on strengthening and restoration of friction surfaces with geomodifiers with the addition of serpentines from the Dashukivka deposit (Ukraine), in particular for heavily loaded nodes.

3. The aim and objectives of the study

The aim of this research is to improve the tribological characteristics of lubricating compositions, in particular their anti-wear and anti-burr properties, which is achieved by adding friction geomodifiers based on natural serpentines to their composition. This will significantly increase the wear resistance and reliability of friction nodes, including heavily loaded ones.

To achieve the goal, the following tasks were set:

– to obtain experimental materials on the effect of friction geomodifiers based on natural serpentines of the Dashukivka deposit on the tribological properties of lubricants when they are used under various conditions, including for heavily loaded nodes;

– to determine the presence of advantages of tribotechnical properties of lubricating compositions with additives of friction geomodifiers based on natural serpentine of the Dashukivka deposit for use in heavily loaded nodes.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our study is the process of improving the tribological characteristics of friction joints, in particular their anti-wear and anti-burr properties.

Numerous studies conducted over the past decades prove the positive effect of FGM additives on the performance of friction nodes but the mechanisms of formation of new structures have not been unequivocally elucidated. For the serpentines of the Dashukivka deposit, this is of a personal nature as they have their own unique composition of trace elements.

The hypothesis of the study is as follows: the introduction of specific functional additives into lubricating compositions, namely friction geomodifiers based on natural serpentines of the Dashukivka deposit, improves their tribological qualities, in particular, anti-wear and anti-burr properties, which leads to an increase in the wear resistance of friction nodes, including heavily loaded ones.

4. 2. Investigated materials and equipment used in the experiment

Serpentine, as a friction geomodifier, when entering the friction zone with increased temperature and pressure, introduces its MgO and SiO_2 molecules into the crystal lattice of the metal. Mg atoms replace Fe atoms, creating a stable protective layer on the metal. Serpentine with a purity of 99.5 % has an average particle size of 1.5 microns (nanocomposite) with a high temperature resistance of 1500–1600 °C. Dielectric. Serpentine is widely present in the clays of the Dashukivka deposit.

The Cherkassy deposit of bentonite clays has five productive horizons. It is not only the largest in Europe but also one of the highest quality in the world – for example, the second horizon is represented by bentonite with a montmorillonite content of up to 95 %.

The average content of microelements in the clays of the Dashukivka section of the Cherkasy deposit is given in Tables 1, 2.

The application of the scanning electron microscopy method made it possible to detect microinclusions in the highly dispersed part of bentonite clay, which are also new formations (Fig. 1, 2) [22]. It is these inclusions that are one of the differences between the serpentines from the Dashukivka area and require research into the effect on tribological processes on the surface structures of parts under conditions of high loads at low friction speeds.

The shape of barite crystals (Fig. 1), taking into account their low strength, suggests that barite crystals were not brought from the weathering crust but formed directly in the main clay mass of the substance (*in situ*). In addition to barite, microinclusions, which are also new formations, were found in the highly dispersed part of the bentonite clay (Fig. 2).

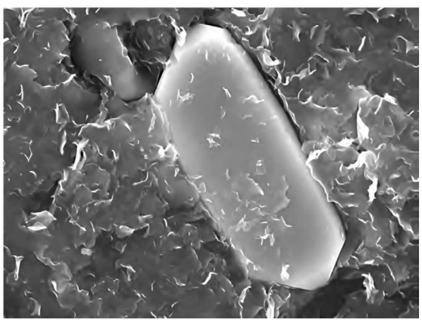
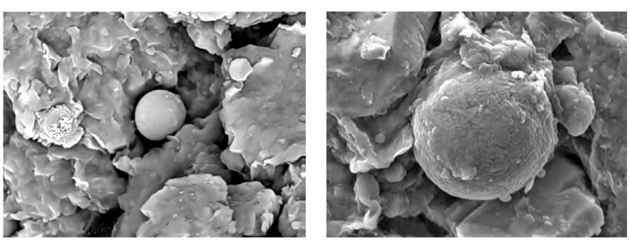


Fig. 1. Barite crystal in bentonite clay (Area of the image viewer field – 1000 μm^2)



a *b*

Fig. 2. Microinclusions in the highly dispersed fraction of bentonites: *a* – spherical particles of allophane in montmorillonite; *b* – titanium-containing particles in montmorillonite

Table 1

The content of individual elements in the barite of Dashukivka bentonite clay according to local X-ray microanalysis

Element	O	Al	Si	S	Ca	Fe	Ba
Mass fraction, %	22.99	4.13	11.0	7.49	0.52	3.83	50.04

Table 2

Chemical composition of Dashukivka bentonite clay, mass share, %

SiO_2	TiO_2	Al_2O_3	Fe_2O_3+FeO	MnO	CaO	MgO	Na_2O+K_2O	P_2O_5	SO_3	SO_2	LAA*
58.8	1.14	17.58	6.3	0.03	2.17	2.16	0.06–0.29	0.05	0.05–0.34	0.19	9.7

*Note: *LAA – loss at annealing*

The surface of these formations is matte, colorless, size 2 – 16 microns. According to the chemical composition, three types of new formations were identified:

1. Allophane-like (Fig. 2, *a*), which consists of, %: SiO_2 – 5.45–9, Al_2O_3 – 26–33, K_2O – 4–6.5, TiO_2 – 0.78–4.05, FeO+Fe_2O_3 – 2.11–7.5, Na_2O – 1.432–13, CaO – to 0.96, MgO – to 2.07.
2. Opal-like, %: SiO_2 – 77–88, Al_2O_3 – 8–20, TiO_2 – to 0.78, FeO+Fe_2O_3 – 1.85–3.54, CaO – to 0.89, MgO – to 1.17.
3. Titanium-containing spherical particles (Fig. 2, *b*), %: SiO_2 – 11–13, Al_2O_3 – 3.8–3.9, K_2O – to 1.13, TiO_2 – 76.6–79.25, FeO+Fe_2O_3 – 4.68–4.86.

The nature of the formation of these particles is currently not clear enough and requires further research.

4. 3. The procedure for determining the physicochemical properties of the sample

To evaluate the efficiency of using lubricating compositions with the addition of FGM based on the serpentine of the Dashukivka deposit, industrial oil I-20 A GOST 20799-88 was used as the base variant. The lubricating composition was created on the basis of one of the most common industrial oils, which does not contain anti-corrosion and antioxidant additives that could change the picture of the effect of FGM on tribological properties. In terms of viscosity, this oil belongs to the "golden mean", that is, it can be used in medium-loaded, medium-speed friction units, in gears, rolling and sliding friction units. The concentration of the additive based on the serpentine of the Dashukivka deposit was 4 wt%. The mixture was made by intensive stirring until the additive was evenly distributed by volume.

In order to obtain acceptable laboratory results of friction and wear tests, research was carried out on the SMC-2 laboratory machine according to the methods of the friction materials research laboratory.

The machine is equipped with an inductive sensor for measuring the moment of friction and an electronic potentiometer for recording it on a paper tape. The MP-62 millivoltmeter with a chromel-koppel thermocouple is used for visual control of the friction temperature.

The tests were stopped after the allotted time or in the event of a creak, which indicated the onset of hardening.

The following quantitative indicators were used:
– moment of friction (coefficient of friction);
– total wear of the tested samples;
– friction surface temperature;
– the temperature of the lubricant;
– effective performance coefficients of additives.

The tests were carried out in the following sequence:

a) we set the specified rotation frequency corresponding to the circumferential speed (it is the sliding speed);

b) for 15 minutes, the test unit was idling to determine the effect of the sliding of the thermocouple on the friction surface on its indicators and to reduce the displacement of the "zero" moment of friction;

c) without stopping the machine, the tested samples were loaded with a specified degree of load, at which the tests were carried out for a certain time.

During the tests, the controlled parameters were load, time, temperature and force (moment) of friction;

d) specific loads in the contact of the tested samples were determined by the materials of the samples and their heat treatment, and the contact area was selected depending on this;

e) the criteria that determined the end of the testing process are as follows:

– a sharp increase in the total wear of the tested samples;

– a sharp increase in the moment of friction;

– a sharp increase in the temperature of the friction surface and the lubricating material;

– the appearance of creaking, grinding or other similar noise.

A variable thermocouple was used to measure the temperature of the friction surfaces.

The tests were carried out under a load of 0 to 1.6 kN to simulate the operating conditions of low-speed, heavily loaded friction units.

The evaluation of the quality of the microstructure of the friction surfaces was carried out on a VHX brand digital microscope (Keyence, USA) at 20–1000× magnification, 4K CMOS, in the Optical Shadow Effect mode, which allows observing and analyzing the smallest surface details. Tribomechanical tests and metallographic studies were carried out on the experimental equipment of Zhejiang XCC Group Co., Ltd (PRC).

5. Results of the study of friction geomodifiers from serpentines of the Dashukivka deposit

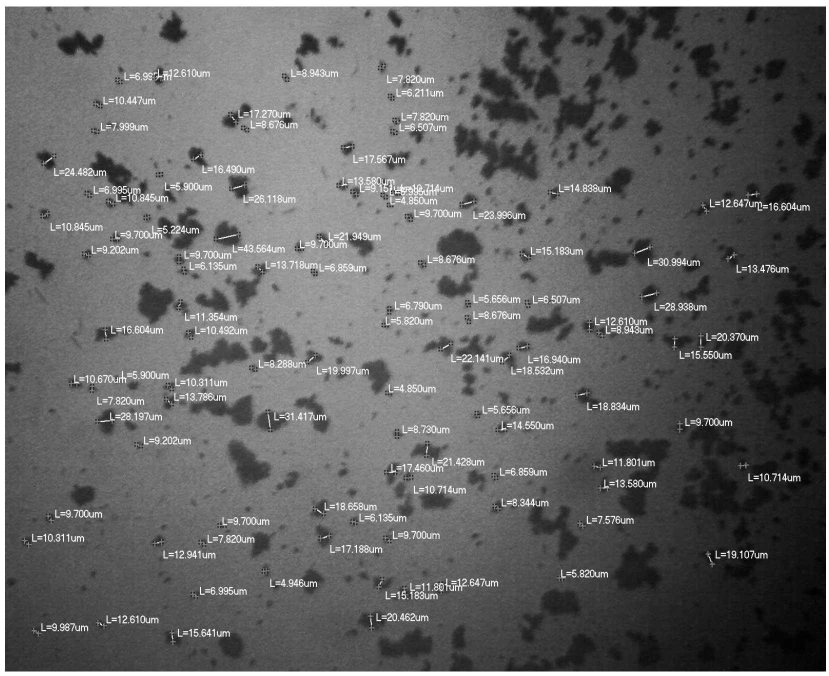
5. 1. Experimental studies of functional indicators of lubricating compositions from serpentines of the Dashukivka deposit

Serpentine of bentonite clays of the Dashukivka deposit is a light gray-yellow powder; density, 2550 kg/m^3; hardness according to the mineralogical scale, 2.5; and formula $Mg_6[Si_4O_{10}](OH_8)$. A photograph of the microstructure of the powder with determination of the size, nature of distribution, and shape of inclusions is presented in Fig. 3, *a*.

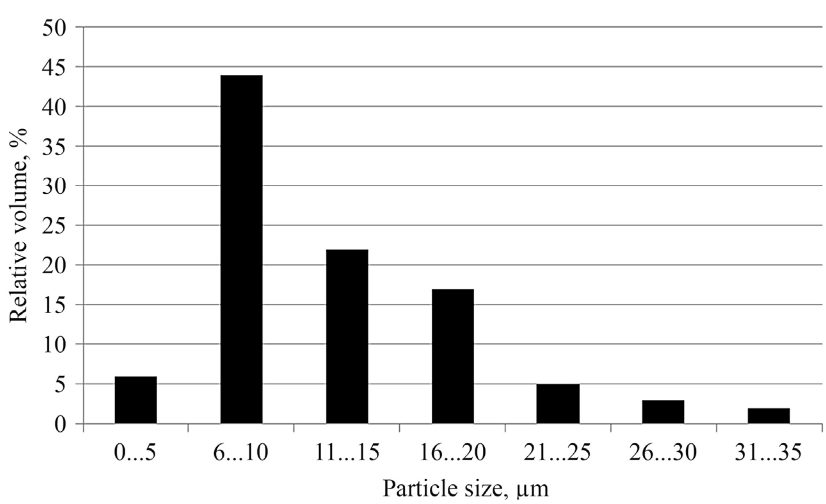
The size of particles in the composition of bentonite according to granulometric analysis is in the interval between fine and very fine powders (according to the size of nanoparticles), and practically does not change from different layers of occurrence in the deposit. The results of the measurements show (Fig. 3, *b*) that the size of most particles lies within 6...10 μm, which is optimal from the point of view of the FGM characteristics.

According to the research program, the primary object of study was the layer on the surface of the contact and the tribological processes related to its formation in the presence of Dashukivka serpentine. The formation of the protective layer can be divided into two phases: the primary structure is formed on the friction surface, the secondary structure is quasi-liquefied, formed from products of tribodestruction of oil and additives, as well as wear products. This formation (the primary structure on the surface of the metal is covered by the secondary structure) shows that the role of the metal is not decisive, and the processes take place with the direct participation of FGM [23–25]. The most sought-after features of FGM coatings are "mirror" purity Ra≈0.07 μm, transparency, high hardness HV=1100–1850 kgf/cm^2, resistance to etching with nitric acid solution, impedance 10–12 Ω/cm, carbon content up to 90 % [26].

When modeling the work of friction pairs, some restrictions were imposed in order to simplify the statement of the problem. For example, the environment and tested materials for the model are kept the same as on the serial parts. During the tests, the controlled parameters were load, time, temperature, and friction moment.



a



b

Fig. 3. Determining the size of particles of the serpentine powder: *a* — photograph of the microstructure 400×; *b* — particle size distribution histogram

The number of necessary repeated measurements is obtained by the formula:

$$n=0.05\ (\sigma_{max}/E)^2, \quad (1)$$

where σ_{max} is the limit value of the error (no more than 10–12 %); E is a probable error, which was set equal to 2–3 %. As a result, n is equal to 2

The temperature that was measured near the friction surface of the stationary element of the steam and should not exceed +150 °C was chosen as a limitation during the tests. The temperature of the samples before the start of each test should not differ by more than ±5 °C from the ambient temperature.

The evaluation of the tested material was based on the analysis of the test results, i.e., on wear resistance, coefficient of friction and temperature near the friction surface. Processing of the test results was carried out in accordance with the accepted dependences.

The coefficient of friction f_{fr} was determined as a fraction of the division of the friction force F measured in the experiment by the total radial load N.

The intensity of wear was determined by the loss of the linear size of the sample related to the friction path:

$$I_L=\frac{\Delta h}{L}, \quad (2)$$

where Δh is linear wear, mm, L is friction distance, km.

The wear of the "disk - disk" pair in this work was estimated by the volume of the worn material, determined by measuring the width of the worn hole using a Brinell magnifying glass (Fig. 4, *a*).

The average intensity of wear was determined by the formula:

$$I_A=\frac{\Delta V}{A}\left(\text{mm}^3/\text{J}\right), \quad (3)$$

where I_A is the intensity of wear, ΔV is volumetric wear, and A is the work of friction forces.

Volume wear was determined by the geometric ratio:

$$\Delta V=S\cdot d=\left(S_1+S_2\right)d=$$
$$=\begin{bmatrix} R_2^2\cdot\arcsin\dfrac{b}{2R_2}-\dfrac{b}{2}\sqrt{R_2^2-\dfrac{b^2}{4}}+ \\ +R_1^2\cdot\arcsin\dfrac{b}{2R_1}-\dfrac{b}{2}\sqrt{R_1^2-\dfrac{b^2}{4}} \end{bmatrix}d, \quad (4)$$

where S – area of figure (Fig. 4, *b*); d – disc width; S_1 – segment area of height h_1; S_2 – segment area h_2.

The work of friction forces was determined by dependence:

$$A=F_{sr}\cdot L, \quad (5)$$

where F_{sr} – friction force at a given load on the friction path L.

The friction path was determined by the formula:

$$L=2\pi R\cdot\omega\cdot t\cdot 10^{-3}, \quad (6)$$

where ω – disk speed; R – radius; t – duration of test.

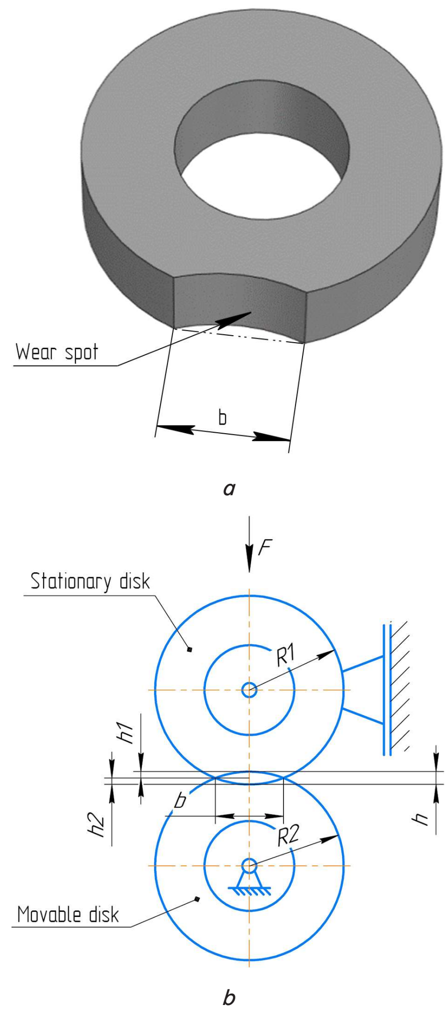


Fig. 4. Scheme for determining the volume of worn material: *a* — the location of the hole on the cylindrical surface of the stationary disk; *b* — scheme for calculating the wear depth

According to the test results, dependences were built:

$$I=f(N),\ \ T_{sr}=f(N),\ \ f_{fr}=f(N),$$

where N is the calculated load on the contact, N; f_{rf} – averaged coefficient of friction, T_{sr} – the highest volume temperature of the element of the friction pair, which is reached during the test, °C; t – test time, min.

The computational and analytical component of the work was used to process experimental data, which were transformed into visual graphic demonstrations using a package of application programs.

The results of tests on wear of friction pairs of steel 45/ShKh15, steel 45/SCh 200, and SCh 200/ SCh 200 in the basic version and with the addition of FGM are shown in Fig. 5, 6.

Materials of friction pairs: steel 45, ShKh15, SCh 200 in various combinations. The roughness of the surfaces of both samples is Ra=0.16 μm, the manufacturing accuracy is IT=7. The rotation frequency of the moving roller ω=16.6±0.33 s^{-1}, which corresponds to the circumferential speed v=2.50±0.1 m/s. The test time is 180 minutes. Load range 200...1600 N.

For the basic version of the "steel 45/ShKh15" pair, exceeding the load of 800 N leads to burrs and seizure of the friction pair. The variant of the mixture with the addition of 4 % FGM increases this resistance to 1600 N, that is, burrs did not occur in the studied range. The rate of wear reaches a maximum at a load of 400 N for the basic version and 600 N for the mixture with FGM additives, but with further increase in the load, a decrease in these indicators is observed.

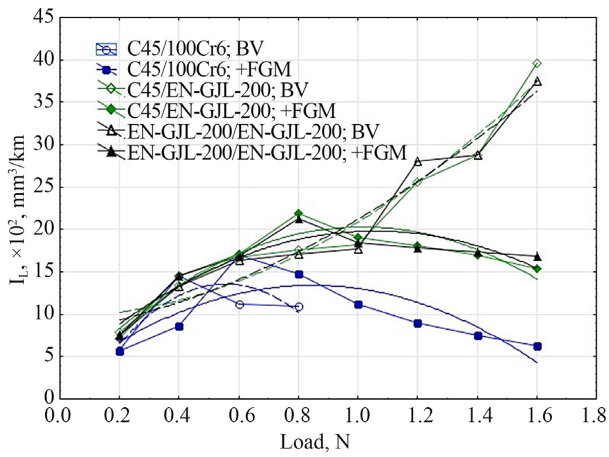


Fig. 5. Plots of wear intensity for pairs “steel 45/ShKh15”, “steel 45/SCh 200” and “ SCh 200/SCh 200” in the basic version and with the addition of friction geomodifiers

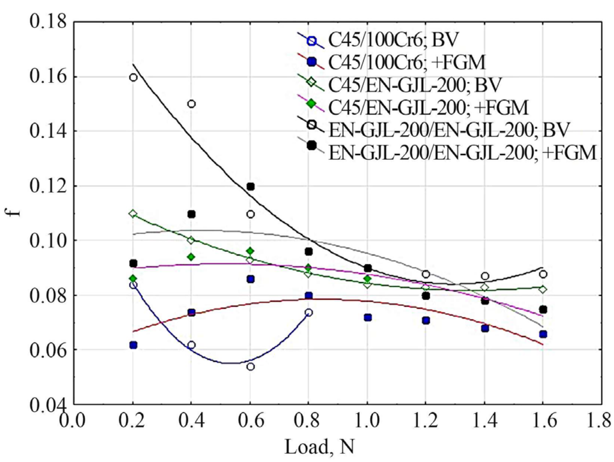


Fig. 6. Dependence of the coefficient of friction on the load when testing pairs of steel 45/ShKh15, steel 45/SCh 200 and SCh 200/SCh 200 in the basic version and with the addition of friction geomodifiers

During tests of cast iron samples in the range of up to 1600 N, burring did not occur both for the basic and for the version with FGM additives, which is probably explained by the antifriction properties of gray cast iron.

One of the determining indicators of the effectiveness of additives is the coefficient of friction. Fig. 6 gives experimental data showing the dependence of the friction coefficient on the load for pairs “steel 45/ShKh15”, “steel 45/SCh 200” and “SCh 200/SCh 200” in the basic version and with the addition of FGM.

At the initial stage of the tests, when the load increased, an increase in the friction moment and friction coefficient was observed, which is probably explained by the abrasive effect of geomodifying particles. The peak load values at which the maximum friction moment and, accordingly, the friction coefficient were observed are 200 N for the basic version and 600 N for the mixture with FGM additives. There is a tendency to decrease the coefficient of friction with increasing load for variants with the addition of a geomodifier.

Research using the methods of selective band diffraction, atomic spectroscopy, confocal Raman spectroscopy [27–30] confirmed that the friction process is accompanied by pyrolysis and carbonization of oils. As a result, RVS-coatings are formed from serpentines, having chemical and physical characteristics similar to *DLC*-films (Diamond Like Coating).Their main elements are carbon C (30...35 %), iron Fe (35...55 %), and oxygen O (5...15 %). Studies of electrical triboprocesses give reasons to believe that the ideas about triboplasma are correct. It is high-temperature triboplasma that leads to the formation of *DLC* films at extreme friction in the presence of carbon-containing lubricants [31, 32].

5. 2. Operational properties of lubricating compositions with additives of geomodifiers from the Dashukivka deposit

The hardness of the friction surface during the specified time of the mechanism determines the efficiency of FGM based on the serpentines. The sintering of powder particles leads to an increase in the hardness of the friction surface, which, in turn, has a favorable effect on its wear resistance.

Studies of changes in the microhardness of the samples after the test cycle were conducted using a PMT-3 microhardness tester. The plot (Fig. 7) shows the evolution of the microhardness of the surface of steel samples (steel 45) under different loads.

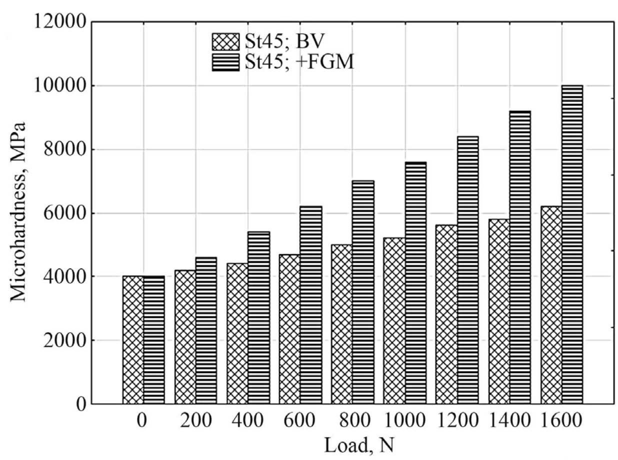
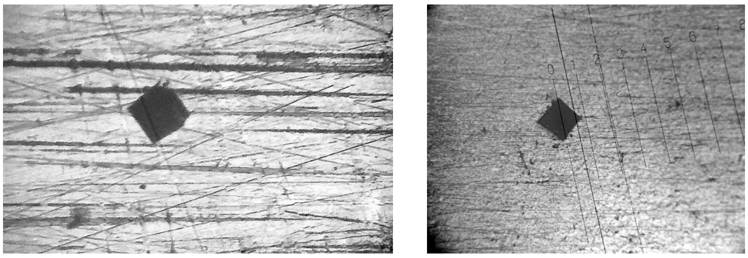


Fig. 7. Transformation of microhardness of tribosurfaces from load

As a result of interaction with the friction surface, nanoparticles of serpentine powder form a stable layer with increased microhardness, which is 1.5–2.5 times higher than the initial microhardness. Increased microhardness has a direct effect on reducing the intensity of wear and, as a result, increasing the service life of the friction unit.

Fig. 8 shows photomicrographs of samples taken after the test cycle.

The absence of streaks and scratches on the friction surfaces of the steel insert (Fig. 8, *b*) is observed, which confirms the absence of abrasive action of solid particles of the serpentine. Coatings have a low coefficient of friction, high strength, hardness and microhardness, thermal conductivity and corrosion resistance. It is necessary to note the particularly high oil-holding capacity of the layer.



a b

Fig. 8. Microphotograph of the surface of the sample with a measuring hole: *a* – basic version; *b* – variant with the addition of friction geomodifiers, ×400

6. Discussion of results of the study of serpentines made of Dashukivka bentonite in heavily loaded friction nodes

The clays of the Dashukivka deposit contain all the elements that are characteristic of serpentines from previously explored quarries. The rock contains MgO and SiO_2, which, according to the theory of geomodification transformations, are further introduced into the crystal lattice of the metal, creating a stable protective layer on the metal. Barite crystals of natural origin are present in bentonite clay. Titanium-containing microinclusions and spherical particles of allophane were detected in montmorillonite (the deposit is a titanium-bearing deposit). All this qualitatively distinguishes the serpentine of the Dashukivka deposit in terms of composition.

Dispersion of the size of the particles and their number in the serpentine can be a disadvantage. The orientation of the process depends on this. It can take place as a strengthening or as an abrasive treatment. The size of most of the particles in the bentonite composition of the Dashukivka deposit, according to the granulometric analysis, meets the requirements and is within 6...10 microns (Fig. 3). It is this dimension that ensures the effectiveness of FGM. And the problem is solved by the selection of bentonite clay precisely from promising parts of the deposit.

Fine particles of the geomodifier fall into local friction zones, where micrometallurgical reactions are initiated due to the action of high temperatures and pressures on the projections of the microrelief. They are accompanied by specific physical and chemical processes at the atomic-crystalline level (exchange reactions of substitution of magnesium atoms for iron atoms).

As a result, modified layers are created on the surfaces of the contacting metals. These layers have a number of specific properties that remain unchanged for a long time. The layers do not have a sharp border with the base metal, have the same coefficient of linear thermal expansion as the metal, do not lose integrity during heating and cooling. They have very high wear resistance and an abnormally low coefficient of friction, slow down the oxidation of the lubricant, thereby increasing its service life. In addition, the layers have dielectric properties, they are fire resistant, resistant to corrosion and oxidation. Separately, their high oleophilicity is noted. The thickness reaches 20...30 μm, the surface roughness decreases to Ra=0.03...0.05 μm.

The addition of 4 % serpentine to the lubricating composition based on I-20 A oil made it possible to reduce the rate of wear by 2–3 times (Fig. 5). The change in the nature of the wear intensity curve is indicative, which confirms the main hypothesis of the formation of repair and restoration coatings on friction surfaces. Immediately after the introduction of geomodifiers, physical and chemical transformations and activation of FGM particles occur during their grinding. At the initial stage, this leads to increased wear and tear. Next, there is "grinding" of the friction surfaces and hardening of the serpentine particles and, as a result, the formation of a protective coating. At the same time, there is an increase in the bearing capacity of the lubricating layer by 2.3 times and a decrease in the coefficient of friction by 2.5–3 times compared to I-20 A without additives (Fig. 6). An increase in the hardness of the surfaces of the friction pairs (material steel 45) was confirmed, the surface microhardness after tests under a load of 1600 N was 6 GPa for the basic version, 10 GPa for the version with FGM additives (Fig. 7).

Control measurements revealed the principle of repair and restoration technology (RVS-technology) (Fig. 8) – reduction of roughness, the absence of deep surface damage. This may indirectly indicate the possibility of ensuring the restoration of parts during operation. Studies prove that such factors (reduction of the friction coefficient and restoration of surfaces) are sufficient conditions for increasing the wear resistance of friction pairs and the mechanism as a whole [33, 34].

A limiting factor may be that FGM showed the greatest effectiveness on surfaces with a high specific load (90...100 MPa). Such conditions are typical for heavily loaded friction pairs (ship fittings, hatch closures). When the friction conditions were softened, the efficiency of FGM decreased. At initial loads (up to 800 N), the introduction of FGM led to an increase in wear intensity compared to the basic version, although it ensured the elimination of seizure of steel samples.

Temporal tribological changes in the layers of the coating, its stability and periodicity of recovery require long-term tests and constant microstructural control with scientific and analytical processing is the direction of further research.

Our results confirm the need to expand scientific research in this area to solve the complex problem of increasing the reliability of tribojunctions.

7. Conclusions

1. We have obtained experimental materials on the effect of friction geomodifiers based on natural serpentines of the Dashukivka deposit on the tribological properties of lubricants. The research was carried out for different materials of friction pairs and under different load conditions: steel 45/ShKh15, steel 45/SCh 200 and SCh 200/SCh 200, load up to 1600 N. Addition of 4 % serpentine to the lubricating composition based on I-20 A oil made it possible to reduce the rate of wear by 2–3 times, and the coefficient of friction by 2.5–3 times compared to the basic version. The introduction of friction geomodifiers into the base lubricant composition causes certain transformational processes. Such transformations have an external manifestation in the form of an increase in surface microhardness from 6 GPa for the basic variant to 10 GPa for the variant with FGM additives.

2. The assessment of tribotechnical properties of lubricating compositions with additives of friction geomodifiers based on natural serpentine of the Dashukivka deposit showed the qualitative advantages of their use specifically

for heavily loaded nodes. An increase in the bearing capacity of the lubricating layer by 2.3 times was noted. For the basic version of the pair steel 45/ShKh15, exceeding the load of 800 N leads to burrs and seizure of the friction pair. The variant of the mixture with the addition of 4 % FGM increases this resistance to 1600 N, i.e., in the studied range no setting occurred. The peak load values at which the maximum friction moment and, accordingly, the friction coefficient were observed are 200 N for the basic version and 600 N for the mixture with FGM additives. There is a tendency to decrease the intensity of wear and the coefficient of friction with increasing load for variants with the addition of a geomodifier. Processes in the surface layers of materials in the contact zone are carried out using repair and restoration technology (RVS-technology), which allows for non-disassembling parts restoration during operation.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

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References

1. Soloviov, S., Bodu, S., Trofymova, O. (2007). Porivnialnyi analiz tekhniko-ekonomichnykh i ekolohichnykh pokaznykiv khimiko-termichnoi obrobky. Tekhnohenna bezpeka. Naukovi pratsi, 61 (48), 74–78. Available at: https://lib.chmnu.edu.ua/pdf/naukpraci/technogen/2007/61-48-12.pdf
2. Solov'ev, S. (2004). Upravlenie nesuschey sposobnost'yu tribosistem metodami makroprofilirovaniya rabochikh poverkhnostey. Problemy trybolohiyi, 2, 10–14.
3. Solov'ev, S., Bodu, S. (2010). K naznacheniyu posadok i zazorov tsilindroporshnevykh sopryazheniy germetichnykh kompressorov. Dvigateli vnutrennego sgoraniya. Vseukrainskiy nauchno-tekhnicheskiy zhurnal, 2, 127–129. Available at: https://repository.kpi.kharkov.ua/handle/KhPI-Press/254
4. Chernets, M., Klimenko, L., Pashechko, M., Nevchas, A. (2010). Tribomekhanika. Tribotekhnika. Tribotekhnologii. Vol. 3. Nikolaev: Izd-vo CHGU im. Petra Mogily.
5. Soloviov, S. M., Bodu, S. Zh. (2012). Pidvyshchennia nesuchoi zdatnosti vazhkonavantazhenykh par tertia. Naukovi pratsi [Chornomorskoho derzhavnoho universytetu imeni Petra Mohyly]. Ser.: Tekhnohenna bezpeka, 203 (191), 27–31. Available at: http://nbuv.gov.ua/UJRN/Npchdutb_2012_203_191_7
6. Chen, W., Gao, Y., Zhang, H. (2009). XPS and SEM Analyses of Self-Repairing Film Formed by Mineral Particles as Lubricant Additives on the Metal Friction Pairs. Advanced Tribology, 660–664. doi: https://doi.org/10.1007/978-3-642-03653-8_215
7. Dolgopolov, K. N., Lyubimov, D. N., Ponomarenko, A. G., Chigarenko, G. G., Boiko, M. V. (2009). The structure of lubricating layers appearing during friction in the presence of additives of mineral friction modifiers. Journal of Friction and Wear, 30 (5), 377–380. doi: https://doi.org/10.3103/s1068366609050134
8. Pogodaev, L. I., Buyanovskii, I. A., Kryukov, E. Yu., Kuz'min, V. N., Usachev, V. V. (2009). The mechanism of interaction between natural laminar hydrosilicates and friction surfaces. Journal of Machinery Manufacture and Reliability, 38 (5), 476–484. doi: https://doi.org/10.3103/s1052618809050124
9. Wang, P., Lv, J., Wang, L. H., Ma, Q., Zhu, X. H. (2011). Research on Tribological Properties of Serpentine Particles as Lubricating Oil Additives. Advanced Materials Research, 284-286, 1001–1005. doi: https://doi.org/10.4028/www.scientific.net/amr.284-286.1001
10. Dolgopolov, K. N., Lyubimov, D. N., Kozakov, A. T., Nikol'skii, A. V., Glazunova, E. A. (2012). Tribochemical aspects of interactions between high-dispersed serpentine particles and metal friction surface. Journal of Friction and Wear, 33 (2), 108–114. doi: https://doi.org/10.3103/s1068366612020031
11. Zhang, J., Tian, B., Wang, C. (2013). Long-term surface restoration effect introduced by advanced silicate based lubricant additive. Tribology International, 57, 31–37. doi: https://doi.org/10.1016/j.triboint.2012.07.014
12. Dunaev, A. V., Zuev, V., Vasilkov, D. V., Lavrov, Y., Pavlov, O. G., Pustovoy, I. F., Sokol, S. A. The hypotheses of mechanisms of action repair serpentine tribopraparatov. Trudy GOSNITI, 112 (2), 134–142. Available at: http://www.oilchoice.ru/download/file.php?id=3797
13. Telukh, D., Kuz'min, V., Usachev, V. (2009). Vvedenie v problemu ispol'zovaniya sloistykh gidrosilikatov v tribosopryazheniyakh. Internet-zhurnal «Trenie, iznos, smazka», 3. Available at: http://www.oilchoice.ru/download/file.php?id=2209
14. Yue, W., Wang, C., Liu, Y., Huang, H., Wen, Q., Liu, J. (2010). Study of the Regenerated Layer on the Worn Surface of a Cylinder Liner Lubricated by a Novel Silicate Additive in Lubricating Oil. Tribology Transactions, 53 (2), 288–295. doi: https://doi.org/10.1080/10402000903420787

15. Qi, X., Jia, Z., Chen, H., Yang, Y., Wu, Z. (2013). Self-Repairing Characteristics of Serpentine Mineral Powder as an Additive on Steel–Chromium Plating Pair under High Temperature. Tribology Transactions, 56 (3), 516–520. doi: https://doi.org/10.1080/10402004.2013.765060
16. Qi, X., Jia, Z., Yang, Y., Fan, B. (2011). Characterization and auto-restoration mechanism of nanoscale serpentine powder as lubricating oil additive under high temperature. Tribology International, 44 (7-8), 805–810. doi: https://doi.org/10.1016/j.triboint.2011.02.001
17. Yuansheng, J., Shenghua, L., Zhengye, Z., He, Y., Feng, W. (2004). In situ mechanochemical reconditioning of worn ferrous surfaces. Tribology International, 37 (7), 561–567. doi: https://doi.org/10.1016/j.triboint.2003.12.005
18. Nan, F., Xu, Y., Xu, B., Gao, F., Wu, Y., Li, Z. (2015). Tribological behaviors and wear mechanisms of ultrafine magnesium aluminum silicate powders as lubricant additive. Tribology International, 81, 199–208. doi: https://doi.org/10.1016/j.triboint.2014.09.006
19. Zhang, B., Xu, B., Xu, Y., Zhang, B. (2011). Tribological characteristics and self-repairing effect of hydroxy-magnesium silicate on various surface roughness friction pairs. Journal of Central South University, 18 (5), 1326–1333. doi: https://doi.org/10.1007/s11771-011-0841-0
20. Yu, H., Xu, Y., Shi, P., Wang, H., Wei, M., Zhao, K., Xu, B. (2013). Microstructure, mechanical properties and tribological behavior of tribofilm generated from natural serpentine mineral powders as lubricant additive. Wear, 297 (1-2), 802–810. doi: https://doi.org/10.1016/j.wear.2012.10.013
21. Yu, H. L., Xu, Y., Shi, P. J., Wang, H. M., Zhang, W., Xu, B. S. (2011). Effect of thermal activation on the tribological behaviours of serpentine ultrafine powders as an additive in liquid paraffin. Tribology International, 44 (12), 1736–1741. doi: https://doi.org/10.1016/j.triboint.2011.06.022
22. Kadoshnikov, V. M., Shekhunova, S. B., Zadvernyuk, H. P., Manichev, V. I. (2013). Authigenic minerals in the bentonite clay of Cherkassy deposit. Mineralogical Journal, 35 (3), 54–60. Available at: http://www.irbis-nbuv.gov.ua/cgi-bin/irbis_nbuv/cgiirbis_64.exe?C21COM=2&I21DBN=UJRN&P21DBN=UJRN&Z21ID=&IMAGE_FILE_DOWNLOAD=1&Image_file_name=PDF/Mineral_2013_35_3_8.pdf
23. De Barros Bouchet, M. I., Kano, M. (2007). Superlubricity of Diamond/Glycerol Technology Applied to Automotive Gasoline Engines. Superlubricity, 471–492. doi: https://doi.org/10.1016/b978-044452772-1/50056-1
24. Erdemir, A., Eryilmaz, O. L. (2007). Superlubricity in Diamondlike Carbon Films. Superlubricity, 253–271. doi: https://doi.org/10.1016/b978-044452772-1/50047-0
25. Fontaine, J., Donnet, C. (2007). Superlow Friction of a-C:H Films: Tribochemical and Rheological Effects. Superlubricity, 273–294. doi: https://doi.org/10.1016/b978-044452772-1/50048-2
26. Yuansheng, J., Shenghua, L. (2007). Superlubricity of In Situ Generated Protective Layer on Worn Metal Surfaces in Presence of $Mg_6Si_4O_{10}(OH)_8$. Superlubricity, 445–469. doi: https://doi.org/10.1016/b978-044452772-1/50055-x
27. Freyman, C., Zhao, B., Chung, Y.-W. (2007). Suppression of Moisture Sensitivity of Friction in Carbon-Based Coatings. Superlubricity, 295–310. doi: https://doi.org/10.1016/b978-044452772-1/50049-4
28. Kano, M. (2015). Overview of DLC-Coated Engine Components. Coating Technology for Vehicle Applications, 37–62. doi: https://doi.org/10.1007/978-3-319-14771-0_3
29. Donnet, C., Erdemir, A. (Eds.) (2008). Tribology of Diamond-Like Carbon Films. Springer. doi: https://doi.org/10.1007/978-0-387-49891-1
30. Nagashima, S., Moon, M.-W. (2015). Diamond-Like Carbon Coatings with Special Wettability for Automotive Applications. Coating Technology for Vehicle Applications, 191–202. doi: https://doi.org/10.1007/978-3-319-14771-0_11
31. Street, K. W., Miyoshi, K., Vander Wal, R. L. (2007). Application of Carbon Based Nano-Materials to Aeronautics and Space Lubrication. Superlubricity, 311–340. doi: https://doi.org/10.1016/b978-044452772-1/50050-0
32. Nakayama, K. (1995). Triboemission And Wear Of Hydrogenated Carbon Films. MRS Proceedings, 409. doi: https://doi.org/10.1557/proc-409-391
33. Balabanov, V. I., Boykov, V. Yu., Balabanova, T. V. (2016). Analyzing repair and reconstructive composites for automotive and tractor mashinery. Agroinzheneriya, 3, 45–52. Available at: https://cyberleninka.ru/article/n/issledovanie-remontno-vosstanovitelnyh-sostavov-dlya-avtotraktornoy-tehniki
34. Olishevska, V., Bas, K., Litvin, P. (2010). Treatment of machines friction connections by nanotribosubstances aт dismantling service. Visnyk Kharkivskoho natsionalnoho avtomobilno-dorozhnoho universytetu, 51, 156–161. Available at: https://cyberleninka.ru/article/n/obrabotka-truschihsya-soedineniy-mashin-nanotribopreparatami-pri-bezrazbornom-servise