Increasing the service life of lubricants for the lubrication of agricultural machinery and road machinery

B V Pokidko, V V Alisin, M N Roshchin and A Yu Simakov

1. Introduction

While exploiting a lubricant, the formation and accumulation of oxidation and decomposition products of organic molecules that make the oil phase are always present. Such a process is accompanied by a decrease in lubricants quality, a drop in durability, deterioration of tribological indicators, increased material consumption, etc. The huge volumes of lubricating oils consumption in agricultural and transport vehicles determine the relevance of research aimed at extending the lubricants life cycle. Various measures are applied to control oil degradation, regeneration and modification of its chemical composition. In recent years, various types of nanoparticle additives have been widely applied to improve lubricants (industrial oils) quality, for example, in various synthetic conditioners, metal-cladding additives, geomodifiers, etc. Nanopowders of diamond-graphite mixtures are used. It was shown in [1] that graphene can be used as a lubricant additive, which is explained by its high mechanical strength and unique layered structure. The difficulty of uniform dispersion of graphene in the base oil is noted due to its low surface energy. Much attention is paid to controlling oils degradation during the friction units operation. The work [2] is devoted to the problems of lubricating oils aging based on the study resonance frequencies transformations in liquid oils. The work [3] reports on the study and development of a method for lubricating oils extraction. In [4] the moisture content in lubricating oil is investigated by spectroscopy in the visible and near infrared range, which makes it possible to quickly and accurately determine the moisture content in the lubricating oil. The aroma content of the oil is an important parameter affecting the quality of lubricating base oils. In [5], a new generalized correlation was developed for determining aromatic substances content, based only on viscosity of the lubricating oil measuring. Much attention is paid [6, 7] to lubricants obtained from biological resources, the use of...
which allows avoiding environmental pollution caused by millions of tons of degraded lubricating oils. However, it should be noted that this focus area is still at the development stage, and currently does not allow switching from petroleum-based oils to vegetable-based oils due to problems associated with reduced fluidity at low temperatures, as well as low oxidation stability. In this regard the work [8] highlights the relevance of processing waste lubricating oil using resources based on antioxidant plant extracts. According to [9] vegetable-based lubricants are used as main components of lubricating fluids due to their high biodegradability and reduced pollutants. Castor oil was found to have the best lubricating properties among vegetable-based oils, but its high viscosity and low fluidity restrict its use in industrial production. It was found that adding nickel micropowder improves the tribological properties of the oil. In work [10] the lubricating properties of liquid oil based on cashew nut shell oil were examined in comparison with base lubricating oil to improve lubrication characteristics in internal combustion engines. In studies of the physicochemical properties of boundary films tribological tests were used [11]. The study of the oil structure and purity was carried out in [12] applying the methods of NMR spectroscopy and high-resolution mass spectrometry. The work determined the thermal and oxidative stability; flash point and pour point; viscosity and viscosity index of the studied oils; and also their tribological and wear resistance properties. The new oils were found to have better oxidation stability than the reference oil. In [13] the encapsulation of nanolayers of tungsten disulfide by the liquid-phase method was carried out in order to improve the distribution of nanoparticles in the base organic lubricating oil. The efficiency of the developed technology was shown using tribological tests. The use of organomodified clay particles as effective additives is well known, as well as their use as adsorbents from non-aqueous media [14, 15], however, a comprehensive consideration of such systems is practically not covered in modern scientific literature and is not available in the Russian-language scientific works, which makes this research relevant both from the theoretical and practical points of view.

The aim of this work is to study the adsorption capacity of aluminosilicate additives used to improve the lubricity and ensure high durability of lubricating compositions, reduce the friction coefficient and increase the wear resistance of lubricated friction surfaces.

2. Materials
The bentonite of the Dash-Salakhlinsky deposit (LLC "Bentonit"), characterized by a relatively high content of montmorillonite (80-85%) and related to swelling anionic clays with a mixed composition of exchangeable cations (mainly sodium cations), the approximate chemical composition of which is given in Table 1, was studied.

|          | SiO₂  | Al₂O₃ | TiO₂ | MgO  | CaO  | Na₂O | K₂O | PP  | Total |
|----------|-------|-------|------|------|------|------|-----|-----|-------|
| Average | 64.8  | 14.6  | 0.95 | 3.34 | 2.91 | 2.31 | 0.52| 5.18| 100.0 |

To obtain the activated and organomodified forms of the sample the following reagents were used: sodium chloride, hydrochloric acid and dialkyldimethylammonium chloride (DADMAC), containing mainly hydrocarbon radicals of the cetyl-stearyl fraction C16-C18 with an average molecular weight of 557 g/mol. Industrial oil of the I20A brand (GOST 20799-88), which is a general-purpose oil, distillate or a mixture of distillate with residual from sulfurous and low-sulfur oils of selective purification, was used as an oil base.

3. Equipment and methods
X-ray diffraction studies were carried out by the X-ray diffraction method using an Ultima IV X-ray diffractometer (Rigaku company) (40 kV, 40 mA); experimental data were processed using the specialized program Jade-6.5. Adsorption measurements were made by the gravimetric method on an
automatic vacuum adsorption unit "Gravimat-4303" and by the volumetric method at -196°C on ASAP 2020 automatic gas analyzer manufactured by Micromeritics. The cation exchange capacity (CEC in meq / 100 g) of natural and modified particles was estimated by the adsorption method of the cationic dye methylene blue (MB). The particle sizes of the fine bentonite fraction were determined by dynamic light scattering (DLS) using a DelsaNanoC analyzer (Beckman Counter). Acid numbers were determined according to the standard method.

Tribological tests were carried out on a machine for testing materials for friction and wear II 5018 according to the method [14]. For research steel samples (steel 45) in the form of a disc 50 mm in diameter and 12 mm wide were used according to the "roller analogy" scheme with a slip of 20% at a load of 1500 N and an angular speed of 380 rpm. The wear of samples pair was measured after a 2-hour cycle of continuous operation.

Sample preparation: Na⁺-activation of bentonite was carried out according to laboratory technology by 3-fold processing of bentonite in 1M NaCl, followed by washing from excess electrolyte with distilled water in a centrifuge. The organomodification of bentonite was carried out according to the suspension technology using 2% bentonite dispersions (or an isolated fine fraction of bentonite = montmorillonite) by mixing with an aqueous-alcoholic solution of DADMAC in the amount exceeding its CEC. Powdered organobentonite was separated by centrifugation (τ = 10 min, n = 6000 rpm) followed by drying at 65°C and mechanical grinding. Acid-activated bentonite was obtained by treating natural bentonite in a 2% suspension of 1M HCl at 90°C for 2 hours, followed by separation of the powdery product by centrifugation, washing the precipitate from excess acid, drying and grinding. By analogy with standard organobentonite, organomodified acid-activated organobentonite was obtained.

4. Results and discussion
Bentonites are traditionally used as adsorbents having a rather complex crystal structure and, as a consequence, a complex hierarchy of colloidal structures in gas (powders) and liquid media (aqueous dispersions, organosols). Primary particles have a lamellar structure, which in the first order can be approximated by the shape of disks or plates (Figure 1).

![Figure 1. Model of a primary montmorillonite lamellar particle.](image)

In calculating the geometric specific surface of the plate, the thickness of a single plate can be used as a parameter from the X-ray phase analysis, i.e. c = 1.2 nm. Figure 2 shows data on the numerical size distribution of particles in a dilute aqueous dispersion of Na⁺-montmorillonite (a fine fraction of bentonite isolated during the initial sample fractionation). Average hydrodynamic diameters (equivalent sizes) of primary particles have sizes of 50-100 nm, with the particles prone to agglomeration.

![Figure 2. Numerical particle size distribution of 0.05% dispersion of Na⁺-montmorillonite from the Dash-Salakhlinsky deposit.](image)
If we use a single plate thickness obtained from the X-ray phase analysis (figure 3) as a parameter from the montmorillonite model plate, then \( c = 1.2 \) nm. The calculation shows (equation 1) that for \( a = b = 100 \) nm, at a mineral density of 2.5 g / cm\(^3\), the specific surface area will reach 670 m\(^2\) / g.

\[
S_{\rho} = \frac{S}{V \rho} = \frac{2ab + 4bc}{abc \rho} = \frac{2}{c^* \rho} + \frac{4}{a^* \rho} = \frac{2}{\rho}
\]

(1)

Figure 3. Diffractogram of Na\(^+\)-bentonite of the Dash-Salakhlinsky field in the area of small angles (2\(\theta\)). The diffraction maximum - 1.19 nm - corresponds to the interplanar distance along the z-axis (the so-called basal reflection, \( d_{001} \)).

Such a large surface area is not always realized in practice due to particle aggregation, and its availability for adsorption depends on a number of factors: the nature and type of exchangeable cations located in the interlayer space between the primary clay particles. In case of organomodified bentonite particles obtained by the ion exchange reaction, exchangeable inorganic cations are replaced by organic modifier cations (DADMAC). This process is accompanied by hydrophobization of the surface and an increase in the interplanar distance. In this case, a part of the surface ceases to be accessible for the adsorption of cations and nitrogen, but it tends to adsorb polar and non-polar organic molecules and polymers.

Table 2 shows the results of determining various forms specific surfaces of the adsorbent by nitrogen adsorption and cationic dye MB (methylene blue).

Table 2. CEC and surface area determined from the adsorption of the dye MB* and the BET equation.

| Sample                  | CEC, mg-equiv/100 g | \( S_a \) adsorption MB, m\(^2\)/g | \( S_a \) BET, m\(^2\)/g |
|-------------------------|---------------------|-----------------------------------|--------------------------|
| Na-bentonite            | 87.0                | 498                               | 92.3                     |
| Acid-activated Bentonite| 22.3                | 128                               | 144.1                    |
| Organomodified bentonite| 0                   | -                                 | 6.3                      |
| Acid-activated and organomodified bentonite | 0 | - | 42.1 |
The specific surface area is estimated by the equation (2),

$$s_u = A_{\text{max}} \cdot N_A \cdot S_{\text{mg}} \cdot 10^5$$  \hspace{1cm} (2)

where $A_{\text{max}}$ - maximum adsorption, mg-equ/100 g, found by $N_A$ - Avogadro constant and $S_{\text{mg}}$ - the area of the methylene blue molecule, taken equal to $9.5 \times 10^{-18} \text{ m}^2$.

The tables demonstrate the differences in the adsorption capacity of all studied samples. Na⁺-bentonite demonstrates the maximum capacity for ion-exchange adsorption and has the maximum specific surface area in an aqueous medium (in terms of MB). As a result of acid activation, the number of ion-exchange centers decreases 4-fold, this is accompanied by an increase in the surface available for adsorption from the gas phase. As a result of organomodification, the sample becomes hydrophobic and loses its ion-exchange capacity, the surface is occupied by large organic cations, which also prevent adsorption from the gas phase (it becomes thermodynamically unfavorable; nitrogen ceases to penetrate into the adsorbent pores). In case of a sample organomodified after acid activation, the surface available for nitrogen adsorption from the gas phase increases significantly. It should be noted that in the latter two cases, due to the acquisition of hydrophobicity the powders become capable of dispersing in oil media, which is confirmed by visual observations (increase in spontaneous swelling in an I20 oil medium and dynamic light scattering data (no data available).

The demonstrated difference in the adsorption behavior and the difference in the behavior of particles with the ability to disperse in different media (water, hydrocarbon medium) suggest significant differences in the samples behavior when they are used as additives and simultaneously adsorbents in the oil phase. In this regard, an assessment was made of the adsorption capacity of adsorbents in the process of purifying waste industrial oil. The waste I20 was used as a model environment under the assumption that it is possible and reasonable to carry out certain correlations in the future. Table 3 shows the data for determining the acid numbers of the waste I20 before and after the adsorption purification using clay adsorbents at 5% additive content. It is worth noting that this experiment was carried out under obviously non-equilibrium conditions: at room temperature, under static conditions (single mechanical distribution of the adsorbent in oil without prolonged and intensive dispersion) for 1 hour- which means that the obtained figures for the purification of waste oil are evaluative and qualitative, and certainly do not reflect the entire adsorption potential of particles.

**Table 3.** The results of acid numbers (AN) determination in the waste oil I20 before and after adsorption purification using clay adsorbents.

| Sample                              | AN, mgPG/g | Efficiency, % |
|-------------------------------------|------------|--------------|
| Base oil I20A                       | 0.53       |              |
| Na-bentonite                        | 0.30       | 43.0         |
| Acid-activated Bentonite            | 0.42       | 20.4         |
| Organomodified bentonite            | 0.25       | 54.1         |
| Acid-activated and organomodified   | 0.32       | 39.6         |
| bentonite                           |            |              |

The results obtained demonstrate the greater efficiency of the organomodified sample in waste oil purification. In this case, the sample obtained by simultaneous activation and modification demonstrate a lower adsorption capacity even in comparison with the hydrophilic sample (Na⁺-bentonite). It should be noted that in the case of acid-activated samples, the increase in acid numbers may be associated with the contribution of intrinsic acidic hydroxyl groups formed after appropriate treatment on the lateral and external surfaces of the mineral. The data let us make the assumption about an increase in the samples efficiency used as adsorbents for purifying the oil phase with an increase in the compatibility between the medium and the phase, i.e. their proximity in polarity. It should be noted that an increase in the
content of organobentonite over 5% does not lead to a significant additional drop in the acid number. This situation can be explained by an increase in the aggregation of particles in the medium. In addition, a similar phenomenon could be explained by the predominant selective adsorption of some specific components of the oxidized oil phase. Based on the study of the chemical dispersion of natural aluminosilicate powders mechanism, a new modified additive is proposed. In order to check the additive efficiency, comparative laboratory tribological tests of PUMA grease with additives based on modified particles of aluminosilicates were done. Comparison of the lubrication efficiency was made in terms of PUMA grease wear resistance (Figure 4). It has been experimentally found that the introduction of an additive based on modified aluminosilicates into the lubricant increases the wear resistance of steel surfaces up to 4 times.

5. Conclusions
The technology of acid and organo-modification of clay particles has been developed and improved on the basis of available natural bentonite raw materials using cationic modifiers of the DADMAC type, which have the ability to disperse in the oil phase and demonstrate adsorption activity in relation to oxidation products in the waste oil, i.e. at the same time the function of an effective additive and antioxidant, which increases the durability of the lubricant, which is very beneficial not only from an economic, but also environmental point of view.

Experimental samples of high-performance additives to lubricants have been created to reduce the wear of steel surfaces by 3-4 times.

![Figure 4. Results of comparative tests of various lubricants.](image)

1- Puma (base); 2- Puma + 0.5% additive (Innovation Program of the Russian Academy of Sciences 2012); 3- Puma + 0.5% additive (No. 5) with the DADMAC modifier (dried, 0.65 pbw); 4- Puma + 0.5% additive (No. 6) with industrial bentonite BENTON-910, (1.54 pp); 5- Puma + 0.5% additive (No. 7) with organomodified bentonite.

References
[1] Xiaojing Ci, Wenjie Zhao, Jun Luo, Yangmin Wu, Tianhao Ge, Lu Shen, Xiulei Gao and Zhiwen Fang 2019 Revealing the lubrication mechanism of fluorographene nanosheets enhanced GTL-8 based nanolubricant oil Tribology International 138 174-83 https:// doi.org/ 10.1016/ j.triboint.2019.05.044
[2] Florian Patocka, Christoph Schneidhofer, Nicole Dörr, Michael Schneider and Ulrich Schmid 2020 Novel resonant MEMS sensor for the detection of particles with dielectric properties in aged lubricating oils Sensors and Actuators A: Physical 315 12290, https:// doi.org/ 10.1016/ j.sna.2020.112290
[3] Aline Fernandes, Jonas O. Vinhal, Achilles Junqueira Bourdot Dutra and Ricardo J. Cassella 2019
Study of the extraction of Ca, Mg and Zn from different types of lubricating oils (mineral, semi-synthetic and synthetic) employing the emulsion breaking strategy. Microchemical Journal 145 1112-8. https://doi.org/10.1016/j.microc.2018.12.043

[4] Chenyang Liu, Xingjia Tang, Tao Yu, Taisheng Wang, Zhenwu Lu and Weixing Yu 2020 Measurement of moisture content in lubricating oils of high-speed rail gearbox by Vis-NIR spectroscopy. Optik 224 165694 https://doi.org/10.1016/j.ijleo.2020.165694

[5] Mehrkesh A H, Hajimirzaee S and Hatamipour M S 2010 A Generalized Correlation for Characterization of Lubricating Base-oils from Their Viscosities Chinese Journal of Chemical Engineering 18(4) 642-7 https://doi.org/10.1016/S1004-9541(10)60269-8

[6] Yaogang Wang, Changhe Li, Yanbin Zhang, Min Yang, Benkai Li, Dongzhou Jia, Yali Hou and Cong Mao 2016 Experimental evaluation of the lubrication properties of the wheel/workpiece interface in minimum quantity lubrication (MQL) grinding using different types of vegetable oils. Journal of Cleaner Production 127 487-99. https://doi.org/10.1016/j.jclepro.2016.03.121.

[7] Owuna F J, Dabai M U, Sokoto M A et al. 2020 Chemical modification of vegetable oils for the production of biolubricants using trimethylolpropane: A review Egyptian Journal of Petroleum 29(1) 75-82 https://doi.org/10.1016/j.ejpe.2019.11.004

[8] Zzeyani S, Mikou M, Naja J, Bouyazza L, Fekkar G and Aiboudi M 2019 Assessment of the waste lubricating oils management with antioxidants vegetables extracts based resources using EPR and FTIR spectroscopy techniques Energy 180 206-15 https://doi.org/10.1016/j.energy.2019.05.007

[9] Shuming Guo, Changhe Li, Yanbin Zhang, Yaogang Wang, Benkai Li, Min Yang, Xianpeng Zhang and Guotao Liu 2017 Experimental evaluation of the lubrication performance of mixtures of castor oil with other vegetable oils in MQL grinding of nickel-based alloy. Journal of Cleaner Production 140(3) 1060-76 https://doi.org/10.1016/j.jclepro.2016.10.073

[10] Selvamuthukumar M, Harish babu B, et al. 2021 Investigation on the lubricating behavior of cashew nut shell liquid oil as a renewable and reliable petrochemical product Materials Today 44(5) 3583-8 https://doi.org/10.1016/j.mattod.2020.09.458

[11] Maroua Hammami, Ramiro Martins, Mohamed Slim Abbes, Mohamed Haddar and Jorge Seabra 2017 Axle gear oils: Friction behaviour under mixed and boundary lubrication regimes Tribology International 116 47-57 https://doi.org/10.1016/j.triboint.2017.06.028.

[12] Mingjin Fan, Jia Ai, Chenghong Hu, Xin Du, Feng Zhou and Weimin Liu 2019 Naphthoate based lubricating oil with high oxidation stability and lubricity Tribology International 138 204-10 https://doi.org/10.1016/j.triboint.2019.05.039

[13] Zhengquan Jiang, Yujuan Zhang, Guangbin Yang, Chuaping Gao, Laigui Yu, Shengmao Zhang and Pingyu Zhang 2019 Synthesis of oil-soluble WS2 nanosheets under mild condition and study of their effect ontribological properties of poly-alpha olefin under evaluated temperatures Tribology International 138 68-78 https://doi.org/10.1016/j.triboint.2019.05.036.

[14] Alisin V V, Pokidko B V and Simakova G A 2012 New class of lubricants based on stable dispersions of solid nanosized powders Journal of Friction and Wear 33(1) 1-4

[15] Alisin V, Pokidko B, Roschehin M and Simakova G 2020 Lubricants to reduce wear of wheels and rails high-speed rail transport IOP Conference Series: Materials Science and Engineering 919 022032 doi:10.1088/1757-899X/919/2/022032