МАТЕРИАЛОВЕДЕНИЕ В МАШИНОСТРОЕНИИ

UDC 669.018.95

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Received 09 March 2020.

MECHANISM OF FORMATION OF HETEROGENEOUS DISPERSED PHASE OF GREASES WITH PARTICIPATION OF NANOSIZED ADDITIVES AND ITS INFLUENCE ON PROPERTIES OF LUBRICANTS

It is shown that in the case of the formation of the heterogeneous structure of the dispersed phase (DP) of greases, which includes the soap component in the form of a complex salt of high molecular weight and low molecular weight acids and nanosized particles of the additive, a more branched structural framework of the DP is formed due to the presence of the additional crystallization centers in the form of the additive nanoparticles. This provides the improved colloidal stability, the greater load capacity and the higher dropping point of the lubricant. The additive nanoparticles implanted into the fibers of the soap component of the DP strengthen it and the probability of their aggregation is excluded. Using as an example the complex lithium grease modified by nanosized particles of the diamond-graphite charge ШA-A (ShA-A), it is shown that the formation of the DP heterogeneous structure can improve the rheological and tribological characteristics of the grease in comparison with the lubricant of the same component composition, but having a single DP from the lithium complex and modifying nanoparticles ШA-A (ShA-A) that are introduced into the dispersion medium (DM) (oil) separately.

Keywords: *grease, dispersed phase, nanosized additives, heterogeneous structure, rheological and tribological properties*

DOI: https://doi.org/10.46864/1995-0470-2020-3-52-63-70

Introduction. Greases are widely used tribotechnical materials that largely determine the performance of friction units of machines and mechanisms of various functional purposes. The greases are highly structured thixotropic dispersions formed by a three-dimensional structural framework of a DP, in the cells of which a DM is held by capillary, adsorption and other physical bonds. In general, the greases can be considered as two-component colloidal systems, in which the DM (75–95 wt.%) is an oil (mineral, synthetic, vegetable), and the DP (5–25 wt.%) is a solid thickener, which can be salts of high molecular weight carboxylic acids (soap), solid hydrocarbons (paraffin, ceresin, etc.), highly dispersed inorganic (silica gel, bentonites, graphite, etc.) and organic (soot, pigments, polymers, urea derivatives, etc.) materials with a well-developed specific surface, capable of structure formation. The most common thickener is the salt of fatty acids (soap), more than 80 % of greases are produced on soap thickeners, which in comparison with other classes of ionic surfactants (sulfonates, alkylsalicylates, etc.) are characterized by low polarity. This largely determines their micelle and structure formation in hydrocarbon liquids. To improve various functional properties (heat resistance, score resistance, wear resistance, etc.), fillers in the form of additives (oil-soluble substances) or additives (oil-insoluble fine solid components, such as graphite powders, molybdenum disulfide, soft metals, etc.) are introduced into the greases [1, 2].

The formation of the structure of the grease DP is a multi-step process that depends on many conditions of formation of the crystal nuclei (associates and micelles), their growth (aggregation of micelles and formation of supramicellar structures — fibers), and, finally, on the conditions for the formation of three-dimensional structural frame, giving the lubrication plasticity and other characteristic properties. Many of these stages can occur in parallel [3, 4].

The formation of dispersed particles of the thickener and a spatial structure is significantly affected by the type and concentration of soap, the DM nature, the presence of surfactants, their concentration and nature, the temperature of soap crystallization and the rate of melt cooling, the intensity of mixing, homogenization and other conditions of the process. The growth of crystals, their aggregation, adhesion and fiber formation occur through ultra-thin solvate layers of surfactants in their presence or in presence of the DM layers that are firmly connected to the surface of dispersed particles and are an element of the DP, structural framework. Depending on the set of factors listed above, the soap thickener in lubricants can exist in various external modifications, varying degrees of dispersion and anisometry. Electron microscopic, X-ray diffraction and other methods of research have established that the elements of the structural framework of the greases are crystalline particles of petal, needle, plate, filamentary, twisted filamentary, rope-formed and other forms. These particles are microscopic in length and colloidal in thickness or diameter [5]. Complex greases differ in higher dropping point, increased anti-wear, anti-seize and visco-temperature characteristics. In such greases, the thickener is a salt of high molecular weight fatty or hydroxycarboxylic acids, and the stabilizer (complexing agent) is a salt of the same cation of a low molecular weight organic or inorganic acid [6].

Effective modifiers of lubricants are nanoscale additives of various nature, but their introduction into the greases is a significant technological complexity associated with the three-dimensional structure of the DP of greases and the tendency of nanoparticles to aggregate. A promising direction in the field of creating the greases is the development of greases with the so-called heterogeneous DP, which consists of solid elements of various nature, shapes and sizes, including nanosized elements [7].

The purpose of this work is to study the mechanism of formation of heterogeneous DP of greases based on complex salt and fine carbon particles, as well as to study their rheological and tribological properties.

Method of studies. To identify the structure of the grease DP and understand the mechanism of its formation, it is necessary to consider its individual components and study the patterns of physical and chemical processes that occur during the structure formation of heterogeneous DP of the grease. The constituent components of high-molecular greases are salts and mineral (synthetic, vegetable) oils. Salts can be obtained on the basis of animal or vegetable fats, rosin, petroleum acids, high molecular weight natural or synthetic acids, as well as hydroxides of alkaline or alkaline earth metals. Highly dispersed particles of various nature, including carbon particles, can be the modifying components of a soap DP with its heterogeneous structure.

The objects of research were simple lithium and complex lithium greases. The oil base was mineral oil of medium viscosity И-40А (I-40A) (GOST 20799-88) produced by OJSC “Naftan”. The grease DP was formed by salts, a metal cation, and an anion (-s) of acids. In the considered greases, the cation was an alkaline metal of the first group of the periodic system, lithium (Li). For the preparation of salts, its hydroxide was used in the form of a 10 % aqueous solution of $LiOH·H_2O$ (GOST 8595-83). The complex grease contains a complex anion of high and low molecular weight acids. In this case, as a high molecular weight acid, 12-hydroxystearic (12-HoSt) acid (molecular formula $CH_3—(CH_2)_5—CH(OH)—(CH_2)_{10}—COOH$, TU 38.101721-78) was used to produce the grease. The acid contains hydroxyl and carboxyl groups in the molecule that contribute to the formation of internal and intermolecular esters. The length of the molecule is also favorable for the formation of structured fibers of the grease DP. Low molecular weight inorganic boric acid H_3BO_3 (GOST 18704-78) was used as a complexing agent. The combined additive ВНИИ НП-357 (VNII NP-357) (TU 38.401.58.314-2002) served as an antioxidant and anticorrosive additive, which was introduced into all samples in an amount of 0.5 wt.%. All chemical reagents had a classification not lower than “pure”. Dispersed carbon particles in the form of diamond-graphite charge ША-А (ShA-A) produced by Scientific and Production Closed Joint-Stock Company “SINTA” (TU RB 100056180.003-2003), expanded graphite produced by the Belarusian State University and technical carbon containing nanotubes produced by the A.V. Luikov Heat and Mass Transfer Institute of the NAS of Belarus were used to modify the grease and form a heterogeneous DP.

The DP microstructure was analyzed using scanning electron microscopy (SEM) according to the method described in [8]. Rheological and tribological properties of greases were studied using standardized methods, including penetration (according to GOST 5346-78), ultimate strength (according to GOST 7143-73), colloidal stability (according to GOST 7142-74), dropping point (according to GOST 6793-88), effective viscosity (according to

GOST 26581-85), welding load and the load wear index (according to GOST 9490-75). The wear rate of the elements of the friction pair and the friction coefficient were determined by the method described in [9].

Study results and discussion. In general, the formation of soap salts occurs by the following chemical reactions:

- for simple salts:

$$HCOOR + MeOH \rightarrow MeCOOR + H_2O;$$

- for complex salts:

$$HCOOR + HAn + 2MeOH \rightarrow$$
$$\rightarrow MeCOOR[MeAn] + 2H_2O,$$

where HCOOR — the high molecular weight acid; MeOH — the hydroxide of the metal; HAn — the low molecular weight acid; MeCOOR — the simple salt; MeCOOR [MeAn] — the complex salt.

At the same time, it should be noted that for the complex greases, the formation of salts will occur in several stages. In particular, for a complex lithium grease, this process will run the following chemical reactions:

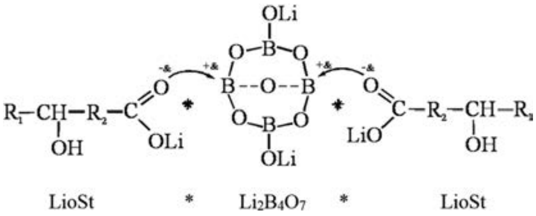
$$\begin{gathered} CH_3{-}(CH_2)_5{-}CH(OH){-}(CH_2)_{10}{-}COOH + LiOH \rightarrow \\ \rightarrow CH_3{-}(CH_2)_5{-}CH(OH){-}(CH_2)_{10}{-}COOLi + H_2O \end{gathered} \quad (1)$$

$$4H_3BO_3 + 2LiOH \rightarrow Li_2B_4O_7 + 7H_2O \quad (2)$$

$$Li_2B_4O_7 + 2LioSt \rightarrow LioSt \cdot Li_2B_4O_7 \cdot LioSt, \quad (3)$$

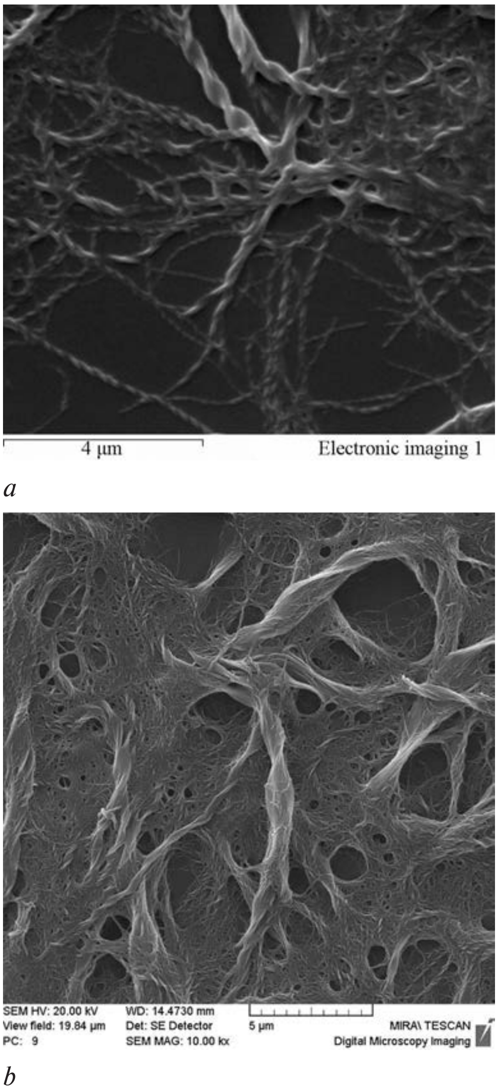
where $LioSt \cdot Li_2B_4O_7 \cdot LioSt$ — complex lithium salt.

The mechanism of formation of a complex lithium salt (*cLi* salt) can be explained as follows. To fill the full octet of the valence shell of boron atoms in the lithium tetraborate $Li_2B_4O_7$ in its electronic shell, two electrons are missing, and the acyl of lithium hydroxystearate LioSt ($CH_3{-}(CH_2)_5{-}CH(OH){-}(CH_2)_{10}{-}COOLi$) has an increased density. Therefore, the components of the *cLi* salt can form a coordination bond of type —B...O—, which is confirmed by the thermal effects accompanying the formation of molecular complexes of lithium tetraborate $Li_2B_4O_7$ with lithium hydroxystearate LioSt. To illustrate this, we can depict the structure of the *cLi* salt molecule in the following form [2, 10]:



(4)

Using SEM tools, images of DP of simple (Litol-24) and complex (ITMOL-150) lithium lubricants were obtained, demonstrating its fibrous structure (Figure 1). At the same time, the primary and secondary structure of the grease DP should be distinguished. The primary structure characterizes the formation of salt molecules into fibers, and the secondary structure characterizes the location of the fibers. From the presented illustrations, it can be seen that the fibers of simple lithium lubricant have the form of twisted threads with a diameter of 0.1—0.5 μm and a length of 10—50 μm, and the fibers of complex lithium lubricant are wider twisted tapes with a length of 10—30 μm and a width of 0.2—2 μm. In both cases, the disordered arrangement of the fibers is clearly visible, in some cases they seem to be intertwined or even fused with each other.



a

b

Figure 1 — Microstructure of the simple (Litol-24) (*a*) and complex (ITMOL-150) (*b*) lithium lubricants

Modifying lubricants with nanosized additives is associated with significant technological difficulties. By simply mixing the additive nanopowder with the base oil, it is usually not possible to obtain homogeneous highly dispersed and colloidally stable suspensions. The reasons for this are mainly the high tendency of nanoparticles to aggregate due to their high surface energy, as well as the residual moisture content of the charge and the hydrophilic nature of the adsorbed impurities on the surface of the nanoparticles, which reduces the energy of interfacial interaction at the interface "solid — oil". When preparing lubricating compositions, in particular with nanosized carbon additives, to increase the interaction energy of charge particles and base oil, preference is given to intensive methods of mechanical (in particular, cavitation) action on carbon oil mixtures in combination with elevated temperatures [11].

However, these methods are unacceptable when nanosized additives are introduced into the composition of greases with a formed DP, which is due to its characteristic three-dimensional structure, which, when applied to intensive mechanical action, will collapse, leading to a sharp deterioration of such indicators as mechanical and colloidal stability, shear strength, penetration, index of destruction and recovery, etc. The second problem that occurs when working with a lubricant containing nanosized additives is that nanoparticles that move freely in its liquid component and are prone to aggregation can form solid abrasive agglomerates under the influence of high local loads and temperatures as a result of coalescing, causing increased wear of the elements of the friction unit.

In the works [12, 13], a method for obtaining a greases modified with nanosized components is proposed, which makes it possible to fix the additive nanoparticles in the fibers of high molecular weight acid salts with the formation of a so-called heterogeneous DP. A distinctive feature of this method of obtaining grease modified with nanocomponents is the preliminary dispersion of aggregates of nanoparticles of the additive in DM (oil) to the required level of their size and subsequent addition to the reactor of components necessary for the synthesis of high molecular weight acid salts. Then the technological process proceeds according to the standard method with the participation of additive nanoparticles in the DP formation.

Introducing nanosized additive aggregates into the DM and vigorously dispersing them, its uniform distribution in the DM is achieved (Figure 2 *a*). After the introduction and melting of high molecular weight acid, its molecules are deposited on the particles of the nanosized additive due to the physicochemical and sorption processes occurring on the surface of the additive nanoparticles and due to the structuring action of electrostatic fields caused by the presence of an uncompensated charge on the surface of the particles. This results in the formation of an isotropic melt in the form of additive nanoparticles with attached acid molecules and unbound acid molecules (see Figure 2 *b*). Then an aqueous solution of alkaline (or alkaline earth) metal hydroxide is introduced into the reaction mass, and the saponification process begins (the formation of a high molecular weight acid salt), while the neutralization reaction involves both unbound acid molecules and acid molecules deposited on the surface of the additive nanoparticles with the implementation of the state schematically shown in Figure 2 *c*. After reaching an isotropic melt, the gelation reaction occurs not only between individual soap molecules (sols), but also with the participation of additive nanoparticles, due to the soap molecules associated with them. In this case, the structural frame fibers are spatially cross-linked by nodal formations containing additive nanoparticles, and a heterogeneous, denser, spatially cross-linked frame is formed from high molecular weight salt fibers and additive nanoparticles (see Figure 2 *d*). Zigzag lines represent fibrous secondary structures (gels) formed during the transformation of primary structures (sols).

The grease obtained by the method [13] differs structurally at the molecular and colloidal levels from the lubricant in which additives are introduced in the traditional way after the formation of the DP structure [14]. This difference is due to the use of nanoscale particles as a technological structure-forming additive, which plays the role of centers of crystallization of the grease DP. In this case, the process of structure formation of the soap DP from salts of high molecular weight acids begins to develop from the surface of the nanoparticles. As a result, nanoparticles are coated with a shell of structured complex salts, and further growth of DP fibers proceeds from the surface of the nanoparticles, they are implanted in the soap thickener of the grease, forming together with it the heterogeneous structure (solid particles of nanoparticles and complex salt), which differs from the structure of the DP of simple soap greases. In this case, a branched fibrous frame of the DP is formed, containing nanoparticles of additives evenly distributed over the entire volume, which do not have the ability to move freely in the DM, which prevents their aggregation and sedimentation in the lubricant.

As a result of using such a technological scheme for obtaining the grease, the following effects may occur:
- obtaining nanoparticles of the required sizes by dispersing their agglomerates in a liquid medium (oil)

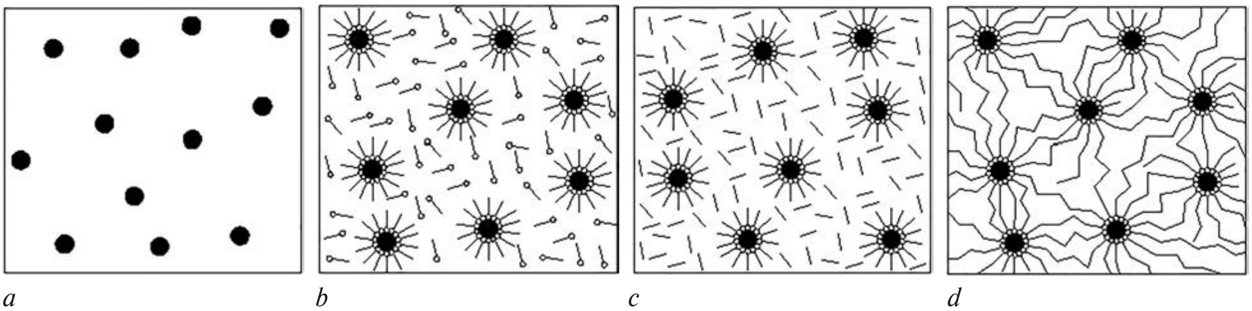


Figure 2 — Scheme of the process of structure formation of heterogeneous DP of the grease in the presence of additive nanoparticles:
a — dispersed additive in the DM; *b* — additive particles with adsorbed acid molecules; *c* — additive after acid neutralization (heterosol); *d* — structured salt molecules with implanted additive nanoparticles (heterogel)

at the initial stage of DP structure formation without destroying the elements of its structure;

- formation of a more branched structural framework of the grease DP due to the structure forming qualities of nanoscale particles;
- stabilization of particles of nanoadditives by their introduction in the DP (Figure 3).

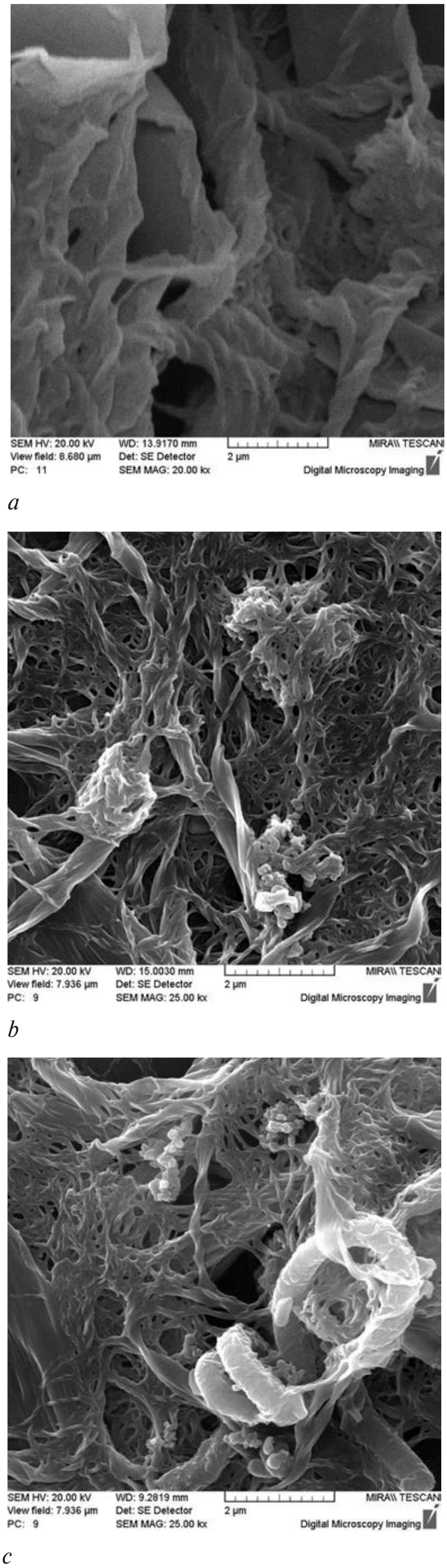
Figure 3 *a* shows that the microstructure of a complex lithium grease with expanded graphite (EG) additives introduced by the method [13] represents mutually embedded EG particles and fibers of a complex lithium salt 12-LioSt·$Li_2B_4O_7$·12-LioSt. EG particles that look like broken plates of a layered structure and 12-LioSt·$Li_2B_4O_7$·12-LioSt fibers are evenly distributed over the analysis area. At the same time, there are no separately located DP elements, the 12-LioSt·$Li_2B_4O_7$·12-LioSt fibers are intertwined with each other, and also braid the EG plates. At the points of contact between the fibers and the plates, they repeat the contours of the plates and are firmly fixed to their surface.

In the coarse-fiber structure of the DP of the complex lithium grease modified with ultradispersed particles of the charge ША-А (ShA-A), the additive particles are completely covered with elements of the soap component of the heterogeneous DP 12-LioSt·$Li_2B_4O_7$·12-LioSt and are inseparable from it (see Figure 3 *b*).

Carbon compounds in the form of nanotubes with a diameter of 50—200 nm and a length of 10—30 µm are fully integrated into the structure of the soap component 12-LioSt·$Li_2B_4O_7$·12-LioSt of the heterogeneous DP of the complex grease obtained by thickening with complex lithium soap and dispersed carbon black particles, they are inseparable from it (see Figure 3 *c*). Due to their shape, nanotubes can act as a structural element of the grease DP and thicken the lubricant.

The rheological properties of plastic lubricants (penetration, colloidal and mechanical stability, dropping point, etc.), as well as their tribological properties (welding load, load wear index, wear index, etc.) depend very significantly on the composition and structure of the DP. The effect of the transition in the composition of DP from simple salts of high molecular weight acids to complex salts of these acids can be seen in the example of calcium and lithium (Table 1) greases. So, if for simple calcium greases the dropping point is 80—100 °C, and the welding load is at the level of 2,100—2,300 N, then for complex calcium greases these indicators are respectively 230—250°C and 3,600—4,000 N. For lithium greases, these indicators have a level of 180—190 °C and 1,200—1,600 N for DP from a simple salt and 230—250 °C and 2,200—2,600 N for DP from a complex salt [15]. Taking into account the above comparison, the use of a complex thickener is more promising for obtaining greases that provide long-term performance of heavy-loaded and high-temperature friction units.

Nanosized additives also have a significant influence on the change in the level of rheological and tri-



a

b

c

Figure 3 — Microstructure of heterogeneous DP of the complex lithium greases containing additives of ultradispersed particles of expanded graphite (*a*), diamond-graphite charge (*b*), carbon nanotubes (*c*)

Table 1 — Indicators of greases Litol-24 and ITMOL-150

Lubricant indicators	Litol-24	ITMOL-150
Thickener	12-LioSt	12-LioSt·$Li_2B_4O_7$·12-LioSt
Penetration, 0.1 mm	235	230
Dropping point, °C	185	230
Viscosity at a temperature of 0 °C and an average gradient of strain rate of 10 s^{-1}, Pa·s	285	280
Shearing strength at a temperature of 20 °C, Pa, not less than	200	205
Colloidal stability, %	12	10
Tribological charactersitics: - welding load, N - load wear index, N	 1,410 280	 2,500 450

bological properties of greases, especially in the case of their impregnation into the structure of the grease DP with the formation of its heterogeneous structure. The Table 2 shows comparative characteristics of the *cLi* grease obtained by the method [13] with modification of the charge ША-А (ShA-A) with nanosized particles and formation of the heterogeneous DP of the composition 12-LioSt·$Li_2B_4O_7$·12-LioSt+ША-А (ShA-A), in comparison with the *cLi* grease with the same amount of the soap thickener 12-LioSt·$Li_2B_4O_7$·12-LioSt and the charge ША-А (ShA-A) made by the method [14] with the introduction of a diamond-graphite charge ША-А (ShA-A) after the DP is formed.

It was found that the grease with a heterogeneous DP of the composition 12-LioSt·$Li_2B_4O_7$·12-LioSt + + ША-А (ShA-A) has higher rheological and tribological characteristics in comparison with a complex lithium grease having a single DP 12-LioSt·$Li_2B_4O_7$·12-LioSt and an additional modified charge additive ША-А (ShA-A). From the test results, it can be seen that with approximately the same penetration rates of both greases (P = (265–270)·10^{-1} mm), the DP heterogeneous structure significantly improves the colloidal stability (oil retention) of the plastic lubricant (from 5.8 to 4.5 %), slightly increases the dropping point (from 232 to 245 °C) and is particularly favorable for tribological properties, increasing the welding load from P_w = 2,450 N to P_w = 3,940 N and the load wear index from LWI = 359 N to LWI = 640 N and reducing the friction coefficient from f = 0.08–0.10 to f = 0.04–0.06 and the wear rate from $I = 3.8\cdot10^{-9}$ to $I = 0.9\cdot10^{-9}$.

Table 2 — Characteristics of *cLi* greases manufactured in various options

Approach	Rheological			Tribological			
	Colloidal stability, %	Penetration P, 10^{-1} mm	Dropping point, °C	Weld load P_w, N	Load wear index LWI, N	Friction coefficient f	Wear rate, I
Method [13]	5.8	270	232	2,450	359	0.08–0.10	$3.8\cdot10^{-9}$
Method [14]	4.5	265	245	3,940	640	0.04–0.06	$0.9\cdot10^{-9}$

Conclusion. Analysis of research results shows that in the case of the formation of heterogeneous structure of the grease DP, comprising a soap component in the form of a complex salt of high molecular weight and low molecular weight acids, and nanoparticles additives, firstly, a more branched DP structural frame is formed due to the presence of additional crystallization centers in the form of nanoparticles additives, which provides greater oil-retaining property and, therefore, improved colloidal stability, higher load capacity and higher dropping point of the grease. Secondly, the additives implanted in the fibers of the DP soap component of a nanoparticle strengthen it, and at the same time the probability of their aggregation is excluded, which together causes increased performance of the lubricant. Thirdly, when the DP structural framework is destroyed as a result of long-term operation, the additive nanoparticles will be released and fall into the friction zone in the active state, retaining their ultra-small size and acting as an anti-friction and anti-seize component of the grease, increasing the overall lifetime of the lubricant.

By the example of the lithium complex lubricant, modified with nanosized particles of diamond-graphite charge ША-А (ShA-A), it is shown that the formation of the DP heterogeneous structure consisting of lithium complex, including the 12-hydroxystearate lithium 12-LioSt and lithium tetraborate $Li_2B_4O_7$, and nanoparticles of the charge ША-А (ShA-A), makes it possible to improve rheological and tribological characteristics of the grease compared with the lubricant of the same component composition but having a single DP from lithium complex 12-LioSt·$Li_2B_4O_7$·12-LioSt and nanoparticles ША-А (ShA-A) separately introduced in the DM (oil). In this case, the colloidal stability changes from 5.8 to 4.5 %, the dropping point increases from 232 to 245°C, the welding load increases by 1.6 times (from P_w = 2,450 N to P_w = 3,940 N), the load wear index increases by 1.8 times (from LWI = 359 N to LWI = 640 N), the friction coefficient decreases by 1.7–2.0 times (from f = 0.08–0.10 to f = 0.04–0.06), and the wear rate of the elements of the friction pair decreases by 4.2 times (from $I = 3.8\cdot10^{-9}$ to $I = 0.9\cdot10^{-9}$).

References

1. Lyubinin I.A., Zheleznyy L.V. Vysokotemperaturnye plastichnye smazki: sostoyanie i perspektivy proizvodstva v stranakh SNG [High-temperature plastic lubricants: condition and production prospects in CIS countries]. *Friction & lubrication in machines and mechanisms*, 2013, no. 7, pp. 30–35 (in Russ.).
2. Ishchuk Yu.L. *Sostav, struktura i svoystva plastichnykh smazok* [Composition, structure and properties of plastic lubricants]. Kiev, Naukovaya dumka Publ., 1996. 510 p. (in Russ.).
3. Afonin V.V., Begar V.A., Kuznetsov V.A., Shibryaev S.B. Issledovanie mezhmolekulyarnykh vzaimodeystviy v smesyakh neftyanykh i sinteticheskikh masel i modeliruyushchikh ikh smesyakh [Research of intermolecular interactions in mixtures of petroleum and synthetic oils and their modeling mixtures]. *Neftekhimiya*, 1990, vol. 30, no. 2, pp. 252–256.
4. Melnikov V.G. Termodinamika mitsellyarnoy sistemy plastichnykh smazok [Thermodynamics of the micellar system of plastic lubricants]. *World of Oil Products. The Oil Companies' Bulletin*, 2007, no. 2, pp. 10–16 (in Russ.).
5. Petrova L.N., Skryabina T.G., Nikonorov E.M., Bakaleynikov M.B. Mikrometody otsenki fiziko-khimicheskikh svoystv plastichnykh smazok [Micromethods for assessment of physico-chemical properties of greases]. *Khimiya i tekhnologiya topliv i masel*, 1987, no. 1, pp. 37–39 (in Russ.).
6. Lyubinin I.A. Sostoyanie i perspektivy proizvodstva plastichnykh smazok v Rossii i stranakh SNG [State and prospects of plastic lubricants production in Russia and CIS countries]. *Khimiya i tekhnologiya topliv i masel*, 2012, no. 1, pp. 3–6 (in Russ.).
7. Vityaz P.A., et al. *Modifitsirovanie materialov i pokrytiy nanorazmernymi almazosoderzhashchimi dobavkami* [Modification of materials and coatings with nanoscale diamond-containing additives]. Minsk, Belaruskaya navuka Publ., 2011. 527 p. (in Russ.).
8. Chekan V.A., Markova L.V., Pinchuk T.I., Ivakhnik A.V. Preparirovanie plastichnykh smazok dlya issledovaniya ikh strukturnogo karkasa metodom skaniruyushchey elektronnoy mikroskopii [Preparation of plastic lubricants for the study of their structural framework by scanning electron microscopy]. *Industrial Laboratory. Diagnostics of Materials*, 2005, no. 8, pp. 36–38 (in Russ.).
9. Karavaev M.G., Kukareko V.A. Avtomatizirovannyy tribometr s vozvratno-postupatelnym dvizheniem [Automated tribometer with reciprocating motion]. *Nadezhnost mashin i tekhnicheskikh sistem*, 2001, vol. 1, pp. 37–39 (in Russ.).
10. Ishchuk Yu.L., Bulgak V.B., Stakhurskiy A.D. Vliyanie sostava kompleksnogo myla na svoystva plastichnykh smazok [Influence of the composition of complex soap on the properties of plastic lubricants]. *Khimiya i tekhnologiya topliv i masel*, 1995, no. 5, pp. 36–37 (in Russ.).
11. Vityaz P.A., Zhornik V.I., Kukareko V.A., Kamko A.I. Formirovanie iznosostoykikh poverkhnostnykh struktur i mekhanizm ikh razrusheniya pri trenii v srede smazochnogo materiala, modifitsirovannogo ultradispersnymi almazografitnymi dobavkami. Chast 1. Tribotekhnicheskie svoystva [Formation of wear-resistant surface structures and their damage mechanism in friction with lubricant modified by ultradispersed diamond-graphite additives. Part 1. Tribological behavior]. *Trenie i iznos*, 2006, vol. 27, no. 1, pp. 61–68 (in Russ.).
12. Zhornik V.I., Ivakhnik A.V. Vliyanie nanorazmernykh uglerodnykh dobavok na strukturu plastichnykh smazok i iznosostoykikh poverkhnostey treniya [Influence of nanoscale carbon additives on the structure of plastic lubricants and wear resistance of friction surfaces]. *Uglerodnye nanostruktury*, 2006, pp. 81–87 (in Russ.).
13. Zhornik V.I., Ivakhnik A.V. *Plastichnaya kompleksnaya litievaya smazka i sposob ee polucheniya* [Plastic complex lithium lubricant and method of its production]. Patent RB, no. 13722, 2008 (in Russ.).
14. Vityaz P.A., Zhornik V.I., Vereshchagin V.A., Gilnich N.E. *Smazochnaya kompozitsiya dlya tyazhelonagruzhennykh uzlov treniya* [Lubricant composition for heavily loaded friction units]. Patent RB, no. 5906, 2004 (in Russ.).
15. Vityaz P.A., Zhornik V.I., Belotserkovsky M.A., Levantsevich M.A. *Povyshenie resursa tribosopryazheniy aktivirovannymi metodami inzhenerii poverkhnosti* [Increasing the lifetime of tribo-coupling by activated methods of surface engineering]. Minsk, Belaruskaya navuka Publ., 2012. 432 p. (in Russ.).

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Поступила в реакцию 09.03.2020.

МЕХАНИЗМ ФОРМИРОВАНИЯ ГЕТЕРОГЕННОЙ ДИСПЕРСНОЙ ФАЗЫ ПЛАСТИЧНЫХ СМАЗОЧНЫХ МАТЕРИАЛОВ С УЧАСТИЕМ НАНОРАЗМЕРНЫХ ДОБАВОК И ЕЕ ВЛИЯНИЕ НА СВОЙСТВА СМАЗОК

Показано, что в случае формирования гетерогенного строения дисперсной фазы (ДФ) пластичных смазочных материалов (ПСМ), включающей мыльную составляющую в виде комплексной соли высокомолекулярной и низкомолекулярной кислот и наноразмерные частицы добавки, образуется более разветвленный структурный каркас ДФ за счет наличия дополнительных центров кристаллизации в виде *наночастиц добавки. Это обеспечивает улучшенную коллоидную стабильность, большую нагрузочную способность и более высокую температуру каплепадения смазки. Имплантированные в волокна мыльной составляющей ДФ наночастицы добавки упрочняют ее, и при этом исключается вероятность их агрегирования. На примере комплексной литиевой смазки, модифицированной наноразмерными частицами алмазно-графитовой шихты ША-А, показано, что формирование гетерогенного строения ДФ позволяет улучшить реологические и трибологические характеристики ПСМ по сравнению со смазкой того же компонентного состава, но имеющей одинарную ДФ из литиевого комплекса и модифицирующие наночастицы ША-А, отдельно введенные в дисперсионную среду (масло).*

Ключевые слова: *пластичный смазочный материал, дисперсная фаза, наноразмерные добавки, гетерогенная структура, реологические и трибологические свойства*

DOI: https://doi.org/10.46864/1995-0470-2020-3-52-63-70

Список литературы

1. Любинин, И.А. Высокотемпературные пластичные смазки: состояние и перспективы производства в странах СНГ / И.А. Любинин, Л.В. Железный // Трение и смазка в машинах и механизмах. — 2013. — № 7. — С. 30–35.
2. Ищук, Ю.Л. Состав, структура и свойства пластичных смазок / Ю.Л. Ищук. — Киев: Наук. думка, 1996. — 510 с.
3. Исследование межмолекулярных взаимодействий в смесях нефтяных и синтетических масел и моделирующих их смесях / В.В. Афонин [и др.] // Нефтехимия. — 1990. — Т. 30, № 2. — С. 252–256.
4. Мельников, В.Г. Термодинамика мицеллярной системы пластичных смазок / В.Г. Мельников // Мир нефтепродуктов. Вестник нефтяных компаний. — 2007. — № 2. — С. 10–16.
5. Микрометоды оценки физико-химических свойств пластичных смазок. / Л.Н. Петрова [и др.] // Химия и технология топлив и масел. — 1987. — № 1. — С. 37–39.
6. Любинин, И.А. Состояние и перспективы производства пластичных смазок в России и странах СНГ / И.А. Любинин // Химия и технология топлив и масел. — 2012. — № 1. — С. 3–6.
7. Модифицирование материалов и покрытий наноразмерными алмазосодержащими добавками / П.А. Витязь [и др.]. — Минск: Беларус. навука, 2011. — 527 с.
8. Препарирование пластичных смазок для исследования их структурного каркаса методом сканирующей электронной микроскопии / В.А. Чекан [и др.] // Заводская лаборатория. Диагностика материалов. — 2005. — № 8. — С. 36–38.
9. Караваев, М.Г. Автоматизированный трибометр с возвратно-поступательным движением: в 2 т. / М.Г. Караваев, В.А. Кукареко // Надежность машин и технических систем. — Т. 1. — Минск: ИТК НАН Беларуси, 2001. — С. 37–39.
10. Ищук, Ю.Л. Влияние состава комплексного мыла на свойства пластичных смазок / Ю.Л. Ищук, В.Б. Булгак, А.Д. Стахурский // Химия и технология топлив и масел. — 1995. — № 5. — С. 36–37.
11. Формирование износостойких поверхностных структур и механизм их разрушения при трении в среде смазочного материала, модифицированного ультрадисперсными алмазографитовыми добавками. Ч. 1. Триботехнические свойства / П.А. Витязь [и др.] // Трение и износ. — 2006. — Т. 27, № 1. — С. 61–68.
12. Жорник, В.И. Влияние наноразмерных углеродных добавок на структуру пластичных смазок и износостойкость поверхностей трения / В.И. Жорник, А.В. Ивахник // Углеродные наноструктуры: сб. науч. тр. — Минск, 2006. — С. 81–87.
13. Пластичная комплексная литиевая смазка и способ ее получения: пат. BY 13722 / В.И. Жорник, А.В. Ивахник. — Опубл. 30.10.2010.
14. Смазочная композиция для тяжелонагруженных узлов трения: пат. BY 5906 / П.А. Витязь, В.И. Жорник, В.А. Верещагин, Н.Е. Гильнич. — Опубл. 30.03.2004.
15. Повышение ресурса трибосопряжений активированными методами инженерии поверхности / П.А. Витязь [и др.]. — Минск: Беларус. навука, 2012. — 432 с.