



Investigation of the structural viscosity of oil films on the friction surface with fullerene compositions

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Abstract

The paper presents theoretical studies of changes in the structural viscosity of oil films on the friction surface with fullerene compositions in the field of action of electrostatic forces of the friction surface and the base lubricant.

A feature of the use of fullerene additives in lubricants is that fullerenes are readily soluble in a wide class of organic and inorganic solvents. At the same time, poor solubility of fullerenes in technical oils (mineral, semi-synthetic and synthetic).

The purpose of this work is to carry out theoretical studies of changes in the structural viscosity of oil films on the friction surface with fullerene compositions in the field of action of electrostatic forces of the friction surface and the base lubricant.

On the basis of the working hypothesis, it was theoretically established that for a thin oil film, located in the field of action of electrostatic forces of the friction surface, it is necessary to consider the structural dynamic viscosity of the lubricant, which at the friction surface has a gel structure, and as the electrostatic forces from the friction surface decrease, the gel structure transforms into the sol structure.

It is shown that the value of the structural viscosity of the considered aggregates is comparable with the viscosity of polymers or bitumen. Moreover, the viscosity of the gel structure is four orders of magnitude higher than the viscosity of the sol structure. An increase in the concentration of fullerenes leads to an increase in the dynamic viscosity of aggregates.

It is theoretically shown that the structure of the oil film, which corresponds to the structure of the gel, belongs to the class of non-Newtonian fluids. With an increase in the sliding speed, the dynamic viscosity of such structures decreases by a factor of 4, which explains the destruction of micelle clusters and the appearance of rotational motions of elastic flocks. It is assumed that this will lead to a decrease in the value of the coefficient of friction. It is shown that for the gel structure, the concentration of fullerenes in the bulk of the base lubricant does not have a large effect on the structural viscosity. Conversely, for the structure of a sol, the concentration of fullerenes has a significant effect on the value of the structural dynamic viscosity.

Key words: fullerenes; oil film; fullerene compositions; structural viscosity; sol structure; gel structure; friction surface electrostatic field; dynamic viscosity

Introduction

A feature of the use of fullerene additives in lubricants is that fullerenes are readily soluble in a wide class of organic and inorganic solvents. At the same time, poor solubility of fullerenes in technical oils (mineral, semi-synthetic and synthetic). To date, the solubility has been determined and analyzed C₆₀ in a lot of liquids. It is shown that the solubility of fullerenes decreases with increasing polarity of the solvent. A number of unusual properties of fullerene solutions have been revealed, so for some solvents the effect of anomalous dependence of the solubility of fullerene on temperature was found. In the technical literature, there are publications that use the preliminary dispersion of fullerenes in solvents, for example, vegetable high oleic oils, and then the introduction of such compositions into technical oils. According to the authors of the work [1], this use of fullerenes gives a better positive effect than the addition of fullerenes in the form of nanopowders to lubricants.

The general structural feature of liquid lubricants in the presence of fullerenes in them is that in the volume of liquid clusters and micelles are formed. Thus, based on the findings [2] it can be argued that a viscous



liquid can be considered as a continuous dispersion medium, clusters and micelles as a dispersion phase. Fullerene molecules that interact with each other and oleic acid molecules of vegetable oil form aggregates, and the viscous liquid medium becomes structured. If the dimensions of the units change over time at a constant flow velocity (sliding), then such a dispersed system is considered thixotropic [2].

Literature review

Author of the work [3] claims that structured fluids form aggregates in the form of doublets or chains, chains can form a continuous grid. The interaction of aggregates in the volume of fluid is expressed in the formation of sufficiently strong compounds, primarily of coagulation origin. Anisometric units (cylinders, disks, ellipsoids) are able to rotate when the layers of liquid are shifted. According to the author of the work [3] the rheological properties of suspensions are determined by the volume concentration of the dispersed phase, the magnitude of the forces of interaction between aggregates and particles and the structure of the formed aggregates. The author considers Brownian motion of particles to be the main factors influencing the process of aggregate formation, gravitational and repulsive forces arising between particles, hydrodynamic interaction between particles.

In our opinion, when considering the processes of friction and wear, when the friction surfaces accumulate electrostatic charge, it is necessary to consider the forces of electrostatic interaction between the units of the dispersed phase and the friction surface. It should be borne in mind that the concentration of units in the field of electrostatic forces of the friction surface will be greater than at a distance from the surface where the field does not act.

According to the conclusions of the work [2] dispersed phase units combined by external forces (in our case electrostatic), in a continuous grid (framework) on the friction surface, acquire the properties of a "solid body".

Minor external forces form an elastic deformation of the frame. At high enough voltages, the frame collapses and the individual units disconnect. In this case, according to the authors [2], individual units (in our case, fullerene molecules) can form a rotational motion between the friction surfaces. When such an interaction mechanism occurs, the viscosity of the fluid gradually decreases [2].

The above conclusion is accepted by us as a working hypothesis of reduction of friction forces in tribosystems in the presence of a dispersed phase in the lubricant, which will be further confirmed by theoretical models and experimentally.

The presence in the volume of the lubricant of the dispersed phase in the form of clusters and micelles requires, along with the total dynamic viscosity of the liquid, to consider the "structural viscosity". This concept was introduced by W. Oswald in 1925 and was further developed in the work of M. Rayner [4]. The use of this concept allows to take into account not only the dynamic viscosity of the liquid, but also the dynamic viscosity of the units that are in the volume of the liquid, taking into account the shear rate.

The authors of the work [5] provides an overview of the literature on lubricants with added nanoparticles. The effect of nanoparticles on the tribotechnical characteristics of oils is analyzed. It is noted in the work that the use of nanoadditives to lubricants leads to an increase in the viscosity of the base medium, high bearing capacity of the interface, reducing the coefficient of friction, increasing wear resistance.

It has been theoretically established that the use of fullerene "solvents", which can be high oleic vegetable oils, can "start" the micelle formation process, where the nucleus of the micelle is a fullerene molecule surrounded by molecules, for example, oleic acid. In works [6, 7] theoretical studies are presented, which showed that the number of micelles is 50 times higher than the number of clusters in the base lubricating medium at the same concentration of fullerenes, and the dipole moment of micelles is an order of magnitude higher than the dipole moment of clusters. At the same time, micelles are more effective, where a single fullerene molecule acts as a nucleus, rather than a cluster of fullerene molecules, which affects the size of the formed micelles. The role of the friction surface on the formation of clusters and micelles in the lubricant film near the friction surface is established. It is shown that under the action of the stress-strain state of the surface layers, the friction surface acts as a "generator of an electrostatic force field", which affects the formation of an electric field in the volume of the oil film. Expressions are obtained for calculating the value of the total electrostatic field strength of the system "friction surface + lubricant".

Purpose

The purpose of this work is to carry out theoretical studies of changes in the structural viscosity of oil films on the friction surface with fullerene compositions in the field of action of electrostatic forces of the friction surface and the base lubricant.

Methods

In developing a microreological model for the formation of a thin film of lubricant on the friction surface under the action of electrostatic forces, the following assumptions were made.

1. The base lubricant is a viscous liquid with a known value of dynamic viscosity at 100°C μ_l , dimension Pa·s.

2. Aggregates of micelles are considered as small rigid spheres. For example, the modulus of elasticity of the fullerene molecule $E_f = (18 - 20) \cdot 10^{11}$ Pa, that is 10 times the modulus of elasticity of steel.

3. The modulus of elasticity of a liquid lubricant is $E_l = 2 \cdot 10^9$ Pa. When a certain amount of fullerenes is introduced into a viscous liquid, which have the value of the elastic modulus $E_f = 18 \cdot 10^{11}$ Pa it is necessary to determine the value of the reduced modulus of elasticity of the lubricant – E_{red} . The value of the reduced modulus of elasticity of such a dispersed medium will be influenced by the concentration of fullerenes in the volume of the lubricant and the value of the intensity of the total electrostatic field of the system "friction surface + lubricant".

4. The dispersion of clusters and micelles in the volume of liquid lubricant outside the electrostatic field of the friction surface is taken as the structure of the sol [4]. In this structure, stresses are perceived by a viscous liquid medium and transmitted to elastic units. This structure has viscoelastic properties.

5. The dispersion of clusters and micelles near the friction surface (in the field of electrostatic forces), take the structure of the gel [6], where between the micelles and the friction surface there are forces of electrostatic interaction, which contribute to the formation of a framework of units, the cavities between which are filled with a viscous fluid. This structure has elastic and viscous properties. Intermicellar forces can relax, respectively, the structure behaves like Maxwell's body [4]. In such a structure, stresses are perceived by the elastic elements of the units and transmitted to a viscous liquid medium.

Results

The value of the reduced modulus of elasticity of such a dispersed medium will be influenced by the concentration of fullerenes in the volume of the lubricant, which can be determined by the following expressions.

Mass concentration of fullerenes per unit mass of lubricant (1 kg) outside the action of the electrostatic field of the friction surface, we express through the dimensionless coefficient:

$$k_f = \frac{M_f}{1000}, \quad (1)$$

where M_f is the fullerene weight, gram;

1000 is the mass of the base lubricant into which fullerenes are introduced, gram.

Therefore, the concentration of the remaining part of the lubricant is expressed through the dimensionless coefficient:

$$k_l = 1 - k_f. \quad (2)$$

The mass concentration of fullerenes per unit of lubricant on the friction surface, i.e. in the field of action of electrostatic forces, we express through the Langevin function, which takes into account that the dipole moment of the dispersed phase aggregates is directed with respect to the field of the friction surface at an angle, which is expressed by the dependence:

$$k_{f,el} = cth(E) - \frac{1}{E}, \quad (3)$$

where E – total intensity of the electrostatic field of the system "friction surface + lubricant", V/m.

We express the concentration of the remaining part of the liquid through the dimensionless coefficient:

$$k_{l,el} = 1 - k_{f,el}. \quad (4)$$

Having obtained dimensionless coefficients that take into account the mass concentration of fullerenes in the lubricant we can write expressions for determining the reduced elastic modulus of the lubricant for the structure of the sol $E_{red,s}$ and gel structure $E_{red,g}$:

$$E_{red,s} = \frac{2 \cdot k_f \cdot E_f \cdot k_l \cdot E_l}{k_f \cdot E_f + k_l \cdot E_l}, Pa, \quad (5)$$

$$E_{red,g} = \frac{2 \cdot k_{f,el} \cdot E_f \cdot k_{l,el} \cdot E_l}{k_{f,el} \cdot E_f + k_{l,el} \cdot E_l}, Pa, \quad (6)$$

Based on the expressions obtained (5) and (6) it is possible to determine the shear modulus of a lubricant if it contains a dispersed phase of a certain concentration outside the action of the field of electric forces of the friction surface – $G_{red,s}$ and near the friction surface, where the field of electrostatic forces acts – $G_{red,g}$:

$$G_{red,s} = \frac{E_{red,s}}{(2 + 2 \cdot \nu_p)}, Pa, \quad (7)$$

$$G_{red,g} = \frac{E_{red,g}}{(2 + 2 \cdot \nu_p)}, Pa, \quad (8)$$

where ν_p is the Poisson's ratio of the dispersed phase is 0,3.

To improve the simulation accuracy, it is necessary to take into account the orientation of the dispersed phase particles outside the action of the forces of the electrostatic field and near the friction surface, where these forces act.

According to the authors of the works [2, 3] dispersed phase aggregates are ellipsoidal. Such aggregates, outside the action of the electrostatic field, can perform rotational movements in the course of the flow of a viscous fluid, and in the field of action of electrostatic forces of the friction surface, they can orient themselves towards the friction surface. This orientation can be taken into account by the angle φ , which is determined between the normal to the friction surface and the main axis of the unit, in the form of an ellipsoid. Taking this angle (in radians) as an average value, you can write an expression to determine the value $tg\varphi$ for sol and gel structures:

$$tg\varphi_s = th(h \cdot 1 \cdot 10^6), \quad (9)$$

$$tg\varphi_g = th(0,12 \cdot h \cdot 1 \cdot 10^6), \quad (10)$$

where h is the thickness of the oil film on the friction surface, which is formed under the action of the field of electrostatic forces of the friction surface, dimension m;

coefficient equal $1 \cdot 10^6$ is a conversion factor, dimension 1/m;

coefficient 0,12 takes into account the presence of a gradient of the electrostatic field strength with distance from the friction surface, we obtained experimentally, the dimensionless quantity.

Based on the above expressions (9) and (10), as well as the formulas given in the works [8, 9], we have obtained expressions for determining the dynamic viscosity of aggregates whose structure consists of Kelvin bodies μ_K and Maxwell bodies μ_M :

$$\mu_K = \frac{G_{red,s}(1 + tg^2\varphi_s)}{\omega \cdot tg\varphi_s}, Pa \cdot s, \quad (11)$$

$$\mu_M = \frac{G_{red,g}(1 + tg^2\varphi_g)}{\omega \cdot tg\varphi_g}, Pa \cdot s, \quad (12)$$

where ω is the frequency of vibrations that are excited by protruding roughnesses on the actual contact spots during sliding is determined by the expression:

$$\omega = \frac{v_{sl}}{d_{acs}}, 1/c, \quad (13)$$

where v_{sl} is the sliding speed, m/s;

d_{acs} is the diameter of the actual contact spot, dimension m.

Based on expressions (11) and (12), which determine the viscosity of aggregates in the form of a Kelvin body and a Maxwell body, we can write an expression for the structural viscosity of the sol μ_s and gel μ_g :

$$\mu_s = k_l \mu_l + k_f \mu_K, \text{ Pa}\cdot\text{s}, \quad (14)$$

$$\mu_g = k_l \mu_l + k_f \mu_M, \text{ Pa}\cdot\text{s}, \quad (15)$$

Dependences of the change in the dynamic viscosity of a thin oil film on the friction surface, which has a sol structure μ_s and gel structure μ_g are shown in fig. 1 and fig. 2.

The nature of the change in the presented dependencies allows us to draw the following conclusions.

1. The value of the structural viscosity of the aggregates under consideration is comparable to the viscosity of polymers or bitumen. In this case, the viscosity of the gel structure is four orders of magnitude higher than the viscosity of the sol structure.

2. The structures under consideration belong to the class of non-Newtonian fluids, since their dynamic viscosity decreases with increasing sliding speed.

3. An increase in the concentration of fullerenes leads to an increase in the dynamic viscosity of aggregates.

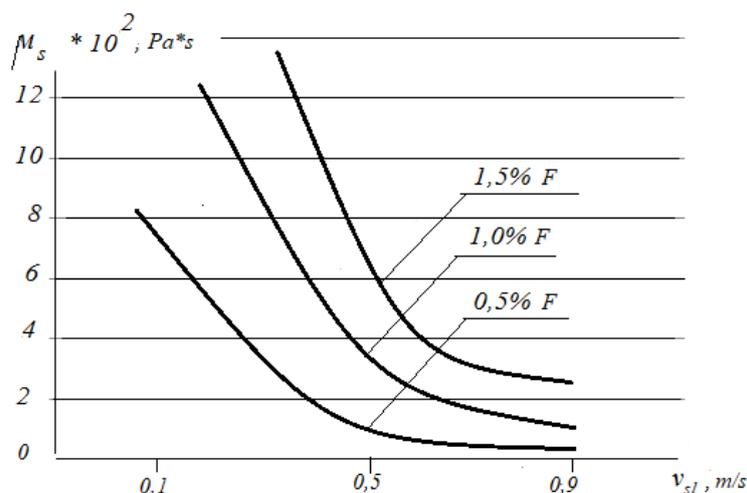


Fig.1. Dependences of the change in the dynamic viscosity of the sol structure on the slip rate and the concentration of fullerenes

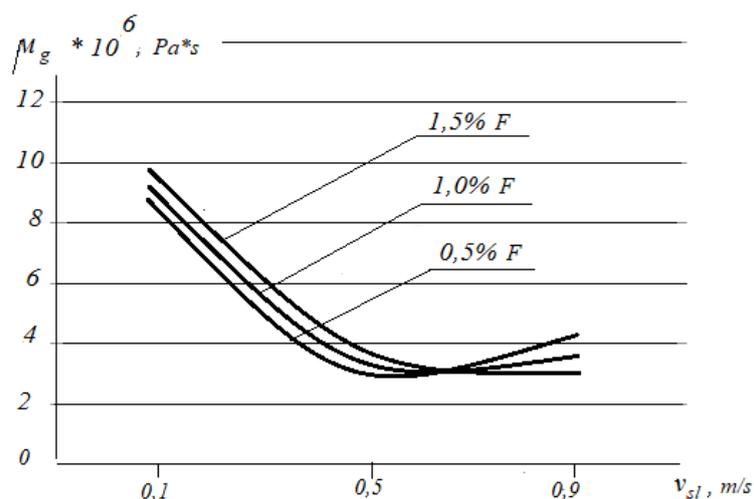


Fig.2. Dependences of the change in the dynamic viscosity of the gel structure on the slip rate and the concentration of fullerenes

As follows from the simulation results for the structures of sol and gel, the properties of a non-Newtonian liquid are inherent. For an oil film on the friction surface, which has a gel structure, fig. 2, dynamic viscosity decreases 4 times with increasing sliding speed. This phenomenon can be explained by the destruction

of aggregates in the form of micelles and the appearance of rotational motion of flocks between friction surfaces [2, 3].

It should be noted that for the gel structure, i.e. for an oil film in the field of action of electrostatic forces of the friction surface, the concentration of fullerenes in the bulk of the base lubricant does not have a large effect. Conversely, for the structure of the sol, fig. 1, the concentration of fullerenes has a significant effect on the value of the dynamic viscosity.

Conclusions

Based on the working hypothesis, it was theoretically established that for a thin oil film located in the field of action of electrostatic forces of the friction surface, it is necessary to consider the structural dynamic viscosity of the lubricant, which has gel structures at the friction surface, and as the electrostatic forces from the friction surface decrease, the gel structure transforms into the sol structure.

The structure of such a film, which corresponds to the structure of the gel, belongs to the class of non-Newtonian liquids. With an increase in the sliding velocity, the dynamic viscosity of such structures decreases by a factor of 4, which is explained by the destruction of clusters and micelles and the appearance of rotational motions of elastic flocks. This will lead to a decrease in the value of the coefficient of friction. These theoretical conclusions will be confirmed by experimental studies and published in our further works.

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Кравцов А.Г. Дослідження структурної в'язкості мастильних плівок на поверхні тертя з фулереновими композиціями

У роботі представлені теоретичні дослідження зміни структурної в'язкості мастильних плівок на поверхні тертя з фулереновими композиціями в полі дії електростатичних сил поверхні тертя і базового мастильного матеріалу.

На підставі робочої гіпотези теоретичним шляхом встановлено, що для тонкої масляної плівки, що знаходиться в полі дії електростатичних сил поверхні тертя, необхідно розглядати структурну динамічну в'язкість мастильного матеріалу, який у поверхні тертя має структур гелю, а в міру зменшення електростатичних сил від поверхні тертя - структура гелю переходить в структуру золю.

Показано, що величина структурної в'язкості розглянутих агрегатів порівнянна з в'язкістю полімерів або бітумів. При цьому, в'язкість структури гелю на чотири порядки вище в'язкості структури золю. Збільшення концентрації фулеренів призводить до збільшення динамічної в'язкості агрегатів.

Теоретичним шляхом показано, що структура мастильної плівки, яка відповідає структурі гелю, відноситься до класу неньютонівських рідин. При збільшенні швидкості ковзання динамічна в'язкість таких структур зменшується в 4 рази, що пояснюється руйнування кластерів і мицелл і появою обертальних рухів пружних флоків. Зроблено припущення, що це призведе до зниження величини коефіцієнта тертя. Показано, що для структури гелю, концентрація фулеренів в об'ємі базового мастильного матеріалу великого впливу на структурну в'язкість не робить. І навпаки, для структури золю, концентрація фулеренів робить істотний вплив на величину структурної динамічної в'язкості.

Ключові слова: фулерени; мастильна плівка; фулеренові композиції; структурна в'язкість; структура золю; структура гелю; електростатичне поле поверхні тертя; динамічна в'язкість