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DEFINITION OF FORMING PROCESSES MICROPARAMETERS FOR EPITROPIC LIQUID CRYSTAL BOUNDARY LUBRICATION LAYERS

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The kinetics theory of ordered boundary lubricating layer formation is presented. The theory contains the description of the formation of boundary lubricating layer from liquid lubricating media containing tribo-active adsorbing component. The expressions for specific forming time and thickness of the boundary lubrication layer in the conditions of the considered model are defined. The prospects of the mentioned parameters experimental definition they are marked out. The tribological efficiency parameter of tribological additive is introduced. This parameter can be evaluated in model physicochemical researches or by molecular modelling methods.

Key words: addition, adsorption, desorption, boundary lubrication layer.

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ОПРЕДЕЛЕНИЕ МИКРОПАРАМЕТРОВ ПРОЦЕССОВ ФОРМИРОВАНИЯ ЭПИТРОПНЫХ ЖИДКОКРИСТАЛЛИЧЕСКИХ ГРАНИЧНЫХ СМАЗОЧНЫХ СЛОЕВ

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В работе рассмотрена кинетическая теория формирования упорядоченных граничных смазочных слоёв. Получено описание процесса формирования граничного смазочного слоя из жидкой смазочной среды, содержащей трибоактивный адсорбирующийся компонент. Определены выражения для характерного времени формирования и толщины граничного смазочного слоя в условиях рассматриваемой модели. Намечены перспективы экспериментального определения указанных параметров. Введен параметр трибологической эффективности присадки, который можно оценивать в модельных физико-химических исследованиях или методами молекулярного моделирования.

Ключевые слова: присадки, адсорбция, десорбция, граничный смазочный слой.

Introduction

Epitropic liquid crystal (ELC) layers appear and exist due to the complex action of superficial long-distance forces and anisotropic molecular interaction in a lubricating material (LM) itself and between LM molecules and solid surface [1]. The presence of such layers and their characteristics provides the required wear resistance of friction couples and lowering the friction coefficient. However, the boundary lubrication layer is not accessible enough for studying *in situ* due to its nature closed for direct research and information about quick dynamic changes of the layer, its thickness and internal structure often is insufficient. In general, the modelling task for forming boundary ordered lubrication layers consists of description of space and time characteristics of the layer and their interaction with molecular structure of the LM surface-active component.

Using amphiphiles of different types as tribo-active LM components, allows one to apply an approach formed in lyotropic liquid crystal theory for layer description [2]. This approach takes into account the superficial nature of lubrication process. A number of factors prevents the universal model of boundary lubrication layer spatial molecular organization to be built: layer thickness inhomogeneity, a variety of molecular forms of possible tribo-active additions, competitive role of solvent, difference of friction couple material properties, orienting (or sometimes disorienting) role of shear processes in layer, etc.

For example, the basic model of boundary lubrication layer structure was proposed by B.V. Deryagin and V.A. Levchenko [3], in which the layer consists of homogenous anisometric molecules of calamitic type mesogen (for example, typical colloid surfactant). According to this model, the ELC phase formation in boundary layer happens under the action of superficial forces. The model describes the contact zone of tribo-coupling (it is an interface filled with ELC layer) as formed out of tribo-active component molecules. The supramolecular organization of adsorption layers located between solid surfaces and ELC-layers is different from the one of ELC layers located farther from the solid surface.

According to the Gibbs' thermodynamic representations, the boundary phase characteristics differ from those of the volume phase. So, the solid surface changes the location of mass centers of ELC lubrication material molecules orienting them homeotropically to the surface border and thus forming the

layer with a quasismectic order (hyperdense packing) and with the orientation order parameter close to one.

The analytical description of the spatial characteristics of the structure consisting of a large number of molecules is highly difficult because of the complicating circumstances mentioned above. However, there is an opportunity to describe the layer taking into considering the kinetics of its formation. Certain specific timing of ordering (the final phase of layer formation) can serve as a characteristic of the polymolecular layer forming process.

As the ELC layer is located between two solid surfaces with evident homeotropic orientation, the vector-direction is the same over the total layer volume. Inducing homeotropic orientation in the ELC layer volume, solid surfaces form homogenous layer order as we can see in the model.

Adsorption of addition molecules plays an important role in the friction process as it creates higher concentration of molecules in the friction contact zone. The forming kinetics and the adsorption layer structure in different aspects studied in detail in [4–6]. In these works, the main attention was paid to the surface structural state and forming mechanisms of adsorption layers at friction surfaces. Changing the composition of the lubrication material was studied in [7]. Following this work, we find interesting to dwell upon the question of lubrication layer formation while changing the composition of lubrication material during friction process.

Problem statement

Under the tribo-active additives, we understand chemical compounds introduced as additions into the LM and able to form physically or chemically adsorbed layers at friction surfaces improving tribo-technical characteristics of the LM. Adsorption kinetics equations describe physicochemical nature of adsorption process and establish the time dependence between concentration of substances in an adsorbent composition and moving phase [8].

Adsorption kinetics of any *i*-component depends on the following main independent factors [9]: concentrations of all components both in LM and in adsorbent composition; parameters defining the diffusion stage of adsorption process (current velocity, temperature and density of moving phase); parameters defining the chemical stage of adsorption kinetics (direct interaction of adsorbent and interacting particles).

The specific feature of the adsorption isotherm equations is the absence of many parameters, which influence the adsorption kinetics. For example, parameters determining diffusion are absent. Adsorption isotherm equations contain only parameters describing the energy of interaction between adsorbate and adsorbent [9]. In the context of the present work we suggest the method of estimating the specific formation time and thickness of a boundary lubrication ELC layer.

The method gives the time parameter of the final lubrication formation stage. For this purpose, we are using a probability pattern of layer formation. Since the creation of a stable connection between molecule and solid surface has a probabilistic nature, the layer formation of one or another structure also can have the probabilistic nature.

Based on the above mentioned it is reasonable to suggest that when adsorption multilayers are being formed, those layers appear in the first place, which structure has the highest formation probability (and the highest probability of bonding between molecules).

The goal of the created model is to estimate the specific forming time τ of the structured layer with thickness h in order to have the opportunity to compare the adsorption time with the specific time parameters of separate stages of friction process.

Theory

Earlier we have studied the problem of changing of tribo-active addition concentration introduced to LM in isothermal friction conditions depending on time [7].

The velocity of the concentration change time of i -tribo-active additive in the LM volume in the case of homogenous materials friction zone under isothermal conditions can be presented as a balance equation:

$$\frac{dC}{dt} = -R_a + R_d - R_t, \quad (1)$$

where R_a – adsorption rate, R_d – desorption rate, R_t – thermal decomposition rate of i -tribo-active additive in LM.

When defining adsorption, desorption and thermal decomposition rates we have taken into account the following assumptions:

- 1) LM is optimized in such a way that additive introduced into it are thermally stable in the applied friction conditions. Therefore, the probability of

chemical decomposition process of addition is low. Thus, the thermal decomposition rate R_t of the addition directs to 0;

- 2) adsorption and desorption rates are directly proportional to the density of active surface adsorption conditions in the friction contact zone N .
- 3) adsorption and desorption rates are directly proportional to the probabilities of adsorption and desorption which in accordance with [10] are approximated with temperature dependencies of the Arrhenius activation dependency type:

$$P_a = K_a e^{-\frac{E_a}{kT}}; P_d = K_d e^{-\frac{E_d}{kT}}, \quad (2)$$

where E_a, E_d – energies of adsorption and desorption activation respectively;

- 4) adsorption rate is directly proportional to the probability that the given active superficial adsorption condition n in the friction contact zone is free, which in its turn is proportional to the current volume concentration of the i -tribo-active addition C ;
- 5) Desorption rate is proportional to the probability that the given active superficial adsorption condition in the friction contact zone n is busy, which in its turn is proportional to the difference between the initial and current volume concentrations of the i -tribo-active addition $(C_0 - C)$.

Based on the above-stated, the adsorption and desorption rates can be presented as:

$$R_a = \alpha N P_a C, \quad R_d = \beta N P_d (C_0 - C), \quad (3)$$

where α and β – dimension factors of adsorption and desorption, respectively.

Taking into account expressions (3) and assumption 1), the concentration isotherm equation (1) will look as:

$$\frac{dC}{dt} = -\alpha N P_a C + \beta N P_d (C_0 - C). \quad (4)$$

Integrating equation (4) with the initial condition $C(t = 0) = C_0$, we will receive the expression for the concentration isotherm of the i -tribo-active addition in the LM volume in the homogenous material friction zone as:

$$C(t) = C_0 \left\{ \frac{\beta P_d}{\alpha P_a + \beta P_d} + \frac{\alpha P_a}{\alpha P_a + \beta P_d} e^{-(\alpha P_a + \beta P_d) N t} \right\} \quad (5)$$

Discussion of results

When the time of friction process is high enough, the dynamic balance of adsorption and desorption processes is set, and as a result the stationary volume concentration of the *i*-tribo-active addition in accordance with equation (5) will be equal to:

$$C_s = C_0 \frac{\beta P_d}{\alpha P_a + \beta P_d}. \quad (6)$$

This value depends on microscopic parameters of adsorption – desorption processes for a particular combination of adsorbent and adsorbate.

Let us introduce a non-dimensional parameter of the tribological activity supply of the *i*-tribo-active additive in the LM volume in the following way:

$$Z = \frac{\alpha P_a + \beta P_d}{\beta P_d}. \quad (7)$$

When optimizing the LM composition based on the concentration parameter of the used tribo-active addition, we need to take into account that its stationary concentration is *Z* times lower than the initial one. The parameter of the addition tribological activity supply is a quantitative probability characteristic of sorption processes. It depends on the physicochemical nature of friction surfaces, additions and specific interaction of addition molecules with matrix lubrication material.

Thus, the concentration isotherm equation (5) taking into account the parameter (7) will be equal:

$$C(t) = C_0 \left\{ \frac{1}{Z} + \frac{Z-1}{Z} e^{-\frac{t}{\tau}} \right\}, \quad (8)$$

where $\tau = \frac{1}{Z\beta P_d N}$ is introduced.

In the equation (8), the first summand is the stationary volume concentration of the addition used. The second summand is the active volume concentration responsible for forming boundary adsorbed molecular layer. This layer lowers the strength of friction interaction.

Parameter

$$\tau = \frac{1}{Z\beta P_d N} \quad (9)$$

is a specific time of lowering of active volume concentration and is a characteristic of forming a boundary lubrication adsorption layer.

In accordance with the equations (2), the tribological activity supply *Z* can be presented as:

$$Z = 1 + \gamma e^{-\frac{E_a - E_d}{kT}}, \quad (10)$$

where $\gamma = \frac{\alpha K_a}{\beta K_d}$ is introduced as micro parameter of dynamic balance for adsorption – desorption processes.

Since there are no convincing proofs that the stationary volume concentration C_s is much lower than the initial concentration C_0 , the second summand in the equation (10) can be expanded into series by the small parameter $\frac{E_a - E_d}{kT}$. Then, the tribological activity supply *Z* will be represented as:

$$Z = 1 + \gamma \left(1 - \frac{E_a - E_d}{kT} \right). \quad (11)$$

The correlations obtained above allow us to study an important practical problem about the thickness of adsorption layer formed at the friction contact zone. When studying the process of forming the adsorption layer, we will proceed from the assumptions 1–5 used before to obtain the concentration isotherm of *i*-tribo-active component (5). In this case, the velocity of layer thickness growth will be defined by two summands:

$$\frac{dh}{dt} = \tilde{\alpha} N P_a C - \tilde{\beta} N P_d (C_0 - C), \quad (12)$$

where the summands $\tilde{\alpha} N P_a C$ and $\tilde{\beta} N P_d (C_0 - C)$ determine the growth rate and decrease of adsorption layer thickness as a result of adsorption and desorption, respectively; $\tilde{\alpha}$ and $\tilde{\beta}$ – dimensional coefficients of adsorption and desorption, respectively.

To solve the differential equation (12) we will use the adsorption isotherm equation (8) obtained above. We will get:

$$\frac{dh}{dt} = \frac{N C_0}{Z} \left\{ (\tilde{\alpha} P_a + \tilde{\beta} P_d) (Z - 1) e^{-\frac{t}{\tau}} + \tilde{\alpha} P_a - (Z - 1) \tilde{\beta} P_d \right\}. \quad (13)$$

From the boundedness condition of the function $h(t)$ follows that the right part of the equation (13) should not contain the constant summand. Therefore, it follows that

$$\tilde{\beta} P_d = \frac{\tilde{\alpha} P_a}{Z - 1}. \quad (14)$$

Taking into account the expression (13), the equation (12) gets a simple representation:

$$\frac{dh}{dt} = N C_0 \tilde{\alpha} P_a e^{-\frac{t}{\tau}}. \quad (15)$$

Integrating the equation (15) with the initial condition $h(t = 0) = 0$, we get the expression for the adsorption layer thickness formed by the *i*-tribo-active addition at friction surfaces:

$$h(t) = NC_0\tilde{\alpha}P_a\tau\left(1 - e^{-\frac{t}{\tau}}\right). \quad (16)$$

Taking into account the expressions (7) and (9), which determine the tribological activity and decreasing time of the addition volume concentration, the expressions (15) and (16) can be represented as:

$$h(t) = \frac{\tilde{\alpha}Z-1}{\alpha Z}C_0\left(1 - e^{-\frac{t}{\tau}}\right). \quad (17)$$

In the long-term working condition of the friction unit with restricted access of lubrication material, the equivalent thickness of lubrication layer is defined (according to (17)) by the following correlation:

$$h = \frac{\tilde{\alpha}Z-1}{\alpha Z}C_0. \quad (18)$$

The experimental determination of the stationary layer thickness (18) by viscosimetric methods and by the method of polarization tribometry is described in detail in [11]. The experimental determination of a non-stationary layer thickness (17) can be obtained by optical methods described in [12].

Conclusions

The approach developed by us allowed not only to model the forming processes of ELC lubrication layers but also experimentally determine the specific time of layer formation using known research methods of lubrication layers. Values of adsorption micro-parameters used for creating models can be obtained by methods of computer and molecular modeling [13], which were recently introduced for solving tribological problems.

Based on the formula for calculating the time of lubrication layer formation, one can conclude that the higher is the factor of addition Z tribological activity, the less time is needed for forming the layer, and the less intensive will be the friction and wear processes. This fact allows us to speak about the parameter Z as about complex criterion of tribological addition efficiency.

Thus, we have come to the more complete description of the forming process of boundary lubrication layer out of liquid lubrication media containing tribo-active adsorbing component. We have introduced the tribological activity factor Z , which can be evaluated in model physicochemical researches. It

should be emphasized that the developed model estimates only the kinetics of layer formation but it is not directly connected with layer characteristics (durability, shifting characteristics, etc.). The latest it requires additional investigations. A significant restriction of the developed approach is evident – the model does not take into account possible chemical reactions of LM components with surface (for example, chemisorption of oxygen diluted in LM).

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