

The Influence of Poly-Molecular Adsorption on the Rheological Behaviour of Lubricating Oil in a Thin Layer

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The explanation and modelling of the impact of anti-wear additives in lubricants at modes and friction characteristics involves considerable difficulties. The experimental studies of many researchers suggest the influence of adsorption of lubricants on the parameters of boundary friction and the hydromechanical characteristics of plain bearings. It is known that the real relationship between the friction coefficient and the contact pressure at these units differs significantly from the theoretical one. Using the example of motor oils, the authors have established the mechanism of action of anti-wear additives and proved the poly-molecular nature of the adsorption of lubricants on the friction pair's surfaces. The authors proposed the rheological model of a thin lubricating film on the basis of physico-chemical concepts about the adsorption mechanism with the influence of the adsorption layer on the viscosity of lubricant near the solid surface. In this paper a method of hydrodynamic calculation of the crankshaft bearings of an internal combustion engine which takes into account the effect of the adsorption of engine oil was developed. The proposed model of the rheological behaviour of the lubricant in a thin layer is based on objective physical and chemical laws and leads to significantly better compliance between the calculation results and the experimental data. Moreover, the elucidation of the mechanism of anti-wear additives action may be useful in the development of lubricants.

Keywords: poly-molecular adsorption, rheological behaviour, rheological model, thin lubricant layer.

1. INTRODUCTION

The behaviour of lubricants in the friction contact has a great influence on the performance of machine parts and mechanisms. It is now known that the rheological behaviour of lubricating oils in thin layers between the friction surfaces is significantly different from that of a normal liquid. For example, the properties of thin layers of motor oils strongly affect the tribological parameters of the sliding bearings of internal combustion engines. The typical dependence of the friction coefficient on contact pressure in the radial sliding bearing or in the similar conformal contact of friction with the lubricant is presented in Figure 1.

An explanation of at least two facts must be given when we are considering the tribological characteristics of friction units. The first is the influence of the presence and amount of anti-wear additives in a region of contact pressure, in which friction has a hydrodynamic character.

If the viscosity of the lubricating oil is constant, anti-wear additives will significantly increase the value of

the contact pressure (P_1 , Fig. 1) at which the minimum friction coefficient is reached. The second fact is the relative constancy of the friction coefficient over a wide range of contact pressure ($P_2 - P_3$, Fig. 1). Both these facts are well known but cannot be explained within the framework of the usual hydrodynamic lubrication theory with the help of well-known theories of boundary friction.

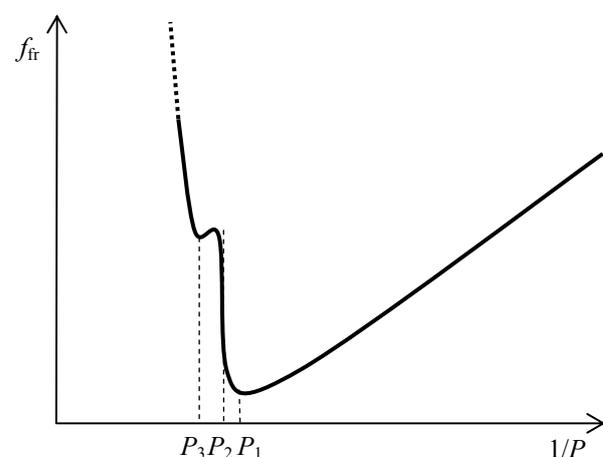


Figure 1. The typical dependence of the friction coefficient on contact pressure in the conformal tribo-units

To describe the rheological behaviour of lubricants in the tribo-unit the change of the state of the fluid during its interaction with the solid surface must be

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considered. Such facts as increased viscosity in liquid layers adjacent to the solid surfaces and the anisotropy of the liquid in these layers can only be explained by poly-molecular adsorption [1-8]. Building an adequate mathematical model of a thin lubricant layer can be performed only on the basis of ideas about the laws of poly-molecular adsorption of hydrocarbon liquids containing surfactants (SAS) with the defined structure.

2. THE FEATURES OF THE ADSORPTION COMPONENTS OF LUBRICANTS ON METAL SURFACES

The creation of a theory of the poly-molecular adsorption of liquids on solid surfaces is an extremely difficult task due to the inadequate development of the physics of fluids. It is generally accepted that the laws of the poly-molecular adsorption of liquids is a consequence of intermolecular interactions and the original structure of the liquid more than the binding energy of the molecules of a liquid with a solid adsorbent [4]. The adsorption of lubricant containing anti-wear additives is a special case since it is caused the secondary adsorption of hydrocarbon molecules on the surface of the monomolecular layer formed by additive molecules. For understanding the adsorption of lubricants and describing the experimental dependencies the adsorption of surfactants, the adsorption of hydrocarbons and the relationship between them should be considered separately.

The adsorption of the zinc dialkyldithiophosphates (ZDDP) and other anti-wear components obeys the usual rules. In particular, the dependence of the mean residence time τ of the surfactant molecules on the metal surface is described by Frenkel's formula:

$$\tau = \tau_0 \exp(Q_a/RT), \quad (1)$$

where: τ_0 is mean residence time of the active center of the molecule on the surface at a temperature $T = 0$; Q_a is the molar heat of adsorption; R is universal gas constant.

One of the distinguishing features of surfactants used as anti-wear additives is the dependence of Q_a on temperature. This dependence is due to the degree of dissociation and the significant difference of adsorption heat of dissociated and undissociated molecules. For example, in the case of zinc dialkyldithiophosphate, the physical adsorption of initial molecules occurs as well as chemical adsorption of the dialkyldithiophosphoric acid. Values Q_a of these processes differ at several times. It results in distinction of τ on some orders [4]. Concentration of the adsorbed molecules of Θ and adsorption ($\Gamma = \Theta/\Theta_{\max}$) on an adsorbent surface usually poorly depends on temperature [2,4] because dependence of a degree of dissociation from the temperature has the exponential form similar to dependence $\tau(T)$.

If activation energy E_a of a chemical reaction of a molecule surfactant with the active sites on a metal surface is rather high, a salutatory increase of Γ at achievement of a particular temperature of activation T_a corresponding to condition $E_a = Q_a(T)$ may happen perhaps.

The tribological properties of some engine oils with thermally activated additives are caused by the presence

of at least two surfactants, one of which has a low heat of physical adsorption and $T_a = 100 - 120$ °C.

The second, more important feature of the monomolecular adsorption layers of anti-wear additives is the impossibility of forming dispersion bonds between the carbohydrate portions of the surfactant molecules due to steric hindrance [1]. Surfactants having an effective diameter of the polar group close to the diameter of the hydrocarbon radical (aliphatic monocarboxylic acids, aliphatic alcohols, amines, etc.), form layers, in which the molecules form hydrocarbon radicals in a packed structure. The insularity of intermolecular bonds within the adsorbed layer leads to a low surface energy and the practical absence of secondary adsorption of hydrocarbons or other components. In contrast, ZDDP and other anti-wear additives with the large size of the polar groups constitute the coordinatively unsaturated adsorption layer whereby the hydrocarbon radicals create a dispersion connection with liquid molecules. For adsorption of gases on the solid surface the specific heat of adsorption q is equal to Q_a per unit area of a monomolecular layer and is made presented in the form of two components [4]:

$$q = q_a + q_x, \quad (2)$$

where: q_a is specific heat due to the energy of association of adsorbate molecules to the surface; q_x is specific heat due to the formation of bonds between molecules of adsorbate inside the layer (lateral cohesion).

When fluid is absorbed, a value q_x is usually small, because of the energy of intermolecular bonds in the liquid and solid phases which are close to each other.

It is obvious that in the adsorption of the hydrocarbon liquid on a surface covered with a dialkyldithiophosphate monolayer, q_a and q_x are identical. In this case the maximum possible value Q is equal to the specific heat of crystallization of the fluid. The real values of the heat of adsorption cannot reach this value due to the reversibility of the adsorption process and the establishment of an equilibrium rate of mass transfer between the adsorbed layer and the adjacent layer of fluid. Thus, the second layer, which is adsorbed on the metal surface and consists of hydrocarbon molecules, is characterized by the lower entropy than the original oil. The entropy of hydrocarbons in a liquid phase differs from the entropy of solid hydrocarbons no more than by 10 %. Energy of dispersion communications can reach from several to ten kJ/mol, i.e., is close to warmth of phase change if a length of hydrocarbon chains is equal $C_{20} - C_{30}$ and coordination numbers are equal 4 – 6. In this case the surface formed by the second layer also has excess energy. It leads to adsorption of the following layer, and so on. In the formation of each subsequent layer the entropy jump occurs on the phase boundary, the value of which decreases for each subsequent layer. Thus, the multimolecular layer is formed. The compensation of the entropy reduction is eventually caused by the chemical bonds “surfactants-metal”. When the temperature increases the balance between processes of adsorption and desorption of hydrocarbon

molecules is displaced towards desorption according to Frenkel's formula (1) because the energy of single intermolecular bonds does not depend on the temperature.

The adsorption of hydrocarbon components is caused by regularities of adsorption and structure surfactant. Its thermodynamic description by means of known theories of poly-molecular adsorption becomes extremely difficult [4]. With only limited success Polyani's theory can be used by representing the poly-molecular layer in the form of sequence of monomolecular layers, each of which contains some share φ_i of the ordered crystal or the solid phase. The entropy of a monomolecular layer can be presented as the sum of the entropy of solid S_s and liquid S_l of phases as a part of this layer

$$S_j = \varphi S_s + (1 - \varphi) S_l. \quad (3)$$

In this case the usual expression of the potential of a force field of the adsorbent

$$\bar{\epsilon} = RT \ln(v_s/v_l), \quad (4)$$

where: v_s and v_l are the molar volumes of the crystal and liquid phases of the adsorbed component, can be presented as

$$\bar{\epsilon} = \Delta\varphi(Q_a + \Delta S), \quad (5)$$

where: $\Delta\varphi$ is the change of share of volume of a crystal phase as a part of the adsorptive layer; ΔS is the entropy difference in the layer directly adjacent to a surface of adsorbent and in liquid on infinite removal from a surface.

The difference in potential of an adsorbent field from the value of a jump of isobaric-isothermal potential ΔG on the interphase border "metal-lubricant" consists in the dependence of the specific heat of adsorption Q_a of the first hydrocarbon layer on the structure of the layer of adsorbed surfactant. Thus, ΔG on the "metal-lubricant" border can be presented as the sum of jump of the potential compensated by adsorption of a dialkyldithiophosphates ΔG_{Sur} , and the jump of the potential compensated by adsorption of hydrocarbons ΔG_{ch} . It is obvious that for the formation of a poly-molecular adsorptive layer a necessary condition is $\Delta G_{ch} > (G_{sol} - G_l)$, where $(G_{sol} - G_l)$ is the difference of isobaric-isothermal potentials for the liquid and solid phases of this hydrocarbon liquid at this temperature. This condition explains anti-wear properties of surfactant which have high warmth of adsorption on the metal surface and form monomolecular layers. Hydrocarbon radicals of these layers form a surface with a rather high energy. In this case we expect a lack of the expressed anti-wear properties at surfactant, similar to an oleic acid. As a rule, the anti-wear additives are used as a surfactant, which is capable of the chemical adsorption with activation energy of a hemo-sorption (E_{aCh}). The activation temperature in this case lies in the range of working temperatures of the tribo-unit. Stable parameters of a boundary layer of lubricant are possible on condition of a transition from the physical adsorption of surfactant to chemical adsorption in the

range of working temperatures, i.e., on condition of $E_{aCh} \approx RT_W$, where T_W is the working temperature of the tribo-unit. In this case the dependence of amount of the adsorbed substance on temperature has the known appearance presented in Figure 2 where: Θ is the concentration of the adsorbed component [mol/m^2]; a is the temperature interval of transition from physical to chemical adsorption; b is an interval of relative stability of the parameters of the dividing lubricant layer in the boundary mode; 1 is process of the physical adsorption of surfactant, $E_{aCh} < RT_W$; 2 is a chemical desorption of surfactant, $E_{aCh} > RT_W$; 3 is concentration of adsorbed surfactant; 4 is the general concentration of the adsorbed molecules, including hydrocarbon components of oil (it is proportional to concentration of adsorbed surfactant).

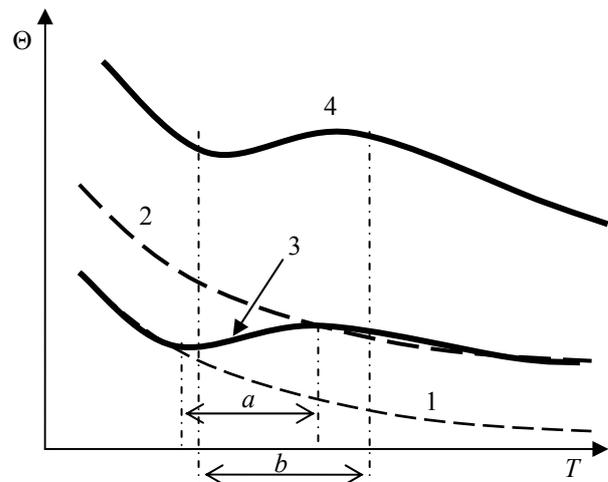


Figure 2. Dependence of Θ on temperature; 1 – concentration of physical adsorption of surfactant; 2 – chemical adsorption of surfactant; 3 – total concentration of surfactant; 4 – general concentration of components of the poly-molecular layer

The condition $E_{aCh} \approx RT_W$ is satisfied for a number of the usual anti-wear components: ZDDP and calcium alkylsalicylates (engine and hydraulic oils), triphenylphosphate and alkyltriaza (oils for guiding slippage), triarylphosphorotrioxides (some plastic lubricants).

3. RHEOLOGICAL MODEL OF A THIN LUBRICANT LAYER

Taking into account the mechanism of formation of a boundary layer, we propose a rheological model which describes the influence of a boundary layer on the range of loadings within which the hydrodynamic mode is realized (P_1 value in Fig. 1) [3,5-8].

The value of viscosity near a surface μ_s is close to the viscosity of solid paraffin. In this case during removal from the metal surface at distance of h_i we will write down the dependence of viscosity $\mu(h)$, as

$$\mu_i = \mu_0 + \mu_s \exp(h_i/l_h) \quad (6)$$

where: μ_s is the parameter representing the conditional value of viscosity at infinitesimal distance from the limiting surface.

In a layer limited by two surfaces, possible distinctions between the adsorptive properties and the structuring influence of various materials need to be

considered. These distinctions are described by parameters l_{h1}, l_{h2}

$$\mu_i = \mu_0 + \mu_s \left(\exp\left(\frac{-h_i}{l_{h1}}\right) + \exp\left(\frac{h_i - h}{l_{h2}}\right) \right). \quad (7)$$

The average (effective) viscosity of the layer and a viscous friction force is expressed as

$$\bar{\mu} = \mu_0 + \frac{\mu_s}{h - h_{s1} - h_{s2}} \cdot \int_{h_{s1}}^{h - h_{s2}} \left(\exp\left(\frac{-h_i}{l_{h1}}\right) + \exp\left(\frac{h_i - h}{l_{h2}}\right) \right) dh_i; \quad (8)$$

$$F = V_0 \left(\left(\frac{\mu_0}{h - h_{s1} - h_{s2}} \right) + \frac{\mu_s}{(h - h_{s1} - h_{s2})^2} \cdot \int_{h_{s1}}^{h - h_{s2}} \left(\exp\left(\frac{-h_i}{l_{h1}}\right) + \exp\left(\frac{h_i - h}{l_{h2}}\right) \right) dh_i \right). \quad (9)$$

where: V_0 is the speed of offset of the surfaces; h_{s1}, h_{s2} are thickness of layers of lubricant on surfaces, the shift speed of which can be considered equal to zero.

Calculation of h_s and l_h is carried out by numerical methods proceeding from (5):

$$\begin{cases} \mu_{ef} = \mu(\mu_0, h, h_s, l_h) \\ F(\mu_{ef}, h_s) = F_{min} \end{cases} \quad (10)$$

The model of the additive interaction of the adsorptive layers (7), (8) and (9) allows us to explain a number of experimental data. It can be also used for an explanation of the dependence of the viscosity of suspensions on the sizes of particles. But this model does not consider the interaction of the adsorptive layers formed on two surfaces. Therefore, it can be applied only at thickness values of the lubricant layer which considerably exceed $2h_s$, i.e. in the presence of a lubricant with the usual viscosity.

At further increase of loading inevitably there is an interaction of the adsorptive layers which character we can describe by using the following considerations:

- The drop of the thermal movement in each layer at distance h_i from a surface, the increase of an enthalpy of intermolecular communications and the accompanying increase of the viscosity can be eliminated by transmission of a moment of the movement as a result of mechanical impact to molecules of this layer. The orderliness of the adsorptive layer can be destroyed by influence of some critical tension of shift. This statement is right and for ideas of liquid crystal structure of a layer.
- It is reasonable to assume that the size of the critical tension of shift depends on the size of an additional enthalpy of the layer and therefore on the initial viscosity μ_i of this layer. As the pressing load increases as a result of rapprochement of surfaces and a fall in the value of $h - 2h_s$, the increase of the shift tension dV/dh

will lead to a reduction of $2h_s$ and to preservation in a clearance of some lubricant layer with the viscosity close to the usual μ_0 , i.e., in some range of loadings $h - 2h_s \approx \text{const}$.

- A mathematical impression of the interaction of the adsorbed layers cannot strictly be gained due to the lack of a description of the liquid condition in the adsorbed layers. The condition $h_s \approx \text{const}$ cannot be considered as strict because of the obvious dependence of the critical value dV/dh on initial (in the absence of slipping) μ_i and, therefore, on h_i .
- For simplification, we accept that $h_{s1} = h_{s2} = h_s$. For an approximate calculation it is necessary to accept a condition that viscosity in the middle of a clearance $\mu(h/2) = \mu_0$.

Considering that at small values $\mu(h/2)$ the value of $\mu_i \rightarrow \mu_0$, expression (7) we replace with

$$\mu_i = \mu_0 + \left[\frac{\mu_s \cdot \mu_0}{\mu_0 + \mu_s \cdot \exp\left(-\frac{h}{2l_h}\right)} \cdot \left(\exp\left(-\frac{h_i}{l_h}\right) + \exp\left(-\frac{h - h_i}{l_h}\right) \right) \right] \quad (11)$$

where:

$$\mu\left(\frac{h}{2}\right) = \mu_s \cdot 2 \exp\left(-\frac{h}{2l_h}\right)$$

is viscosity in a middle part of a layer.

At high values $\mu(h/2)$ the value of the second part tends to zero and the value $\mu_i \rightarrow \mu_0$. For the average viscosity and the power of liquid friction respectively we will find that

$$\bar{\mu} = \mu_0 + \frac{\mu_s}{h - 2h_s} \int_{h_{s1}}^{h - h_{s2}} \frac{\mu_0 \cdot M}{\mu_0 + \mu_s \cdot 2 \exp\left(-\frac{h}{2l_h}\right)} dh_i; \quad (12)$$

$$F = V_0 \left(\left(\frac{\mu_0}{h - 2h_s} \right) + \frac{\mu_s}{(h - 2h_s)^2} \cdot \int_{h_s}^{h - h_s} \frac{\mu_0 \cdot M}{\mu_0 + \mu_s \cdot 2 \exp\left(-\frac{h}{2l_h}\right)} dh_i \right), \quad (13)$$

where:

$$M = \left(\exp\left(\frac{-h_i}{l_{h1}}\right) + \exp\left(\frac{h_i - h}{l_{h2}}\right) \right).$$

4. CONCLUSION

The main engineering objective of hydrodynamic calculations of units of liquid friction is the determination of load ability and speed of wear. To solve this problem

efficient algorithms for calculating and adequate rheological model of the lubricant are needed. The proposed model of the rheological behaviour of lubricant in a thin layer is based on objective physical and chemical laws and achieves significantly better correspondence of calculation results with experimental data.

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УТИЦАЈ ПОЛИМОЛЕКУЛАРНЕ АДСОРПЦИЈЕ НА РЕОЛОШКО ПОНАШАЊЕ ТАНКОГ СЛОЈА УЉА ЗА ПОДМАЗИВАЊЕ

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Објашњење и приказивање утицаја који адитиви за смањење хабања у мазивима имају на врсту подмазивања и карактеристике трења је доста сложено. Експериментална испитивања многих истраживача указују да постоји утицај адсорпције мазива на параметре трења при граничном подмазивању, односно на хидродинамичке карактеристике клизних лежајева. Познато је да се стварна веза између коефицијента трења и контактнoг притиска код ових елемената значајно разликује од теоријске. Аутори овог рада су на примеру моторних уља установили механизам деловања адитива за смањење хабања и доказали полимoleкуларну природу адсорпције мазива на контактне површине. Предложен је реолошки модел за танак слој мазива на основу физичко-хемијског концепта механизма адсорпције, који подразумева утицај адсорбованог слоја на вискозност мазива у близини површина које се подмазују. Разрађен је и метод хидродинамичког прорачуна лежаја коленастог вратила мотора СУС који узима у обзир ефекат адсорпције моторног уља. Предложени модел реолошког понашања танког слоја мазива је заснован на постојећим хемијским и физичким законима, а даје знатно бољу сагласност између прорачунатих и експерименталних резултата. Поред тога, дато објашњење механизма деловања адитива за смањење хабања може да буде корисно и у развоју нових мазива.