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RESEARCH

Study of Effect of Metal Oleates on Mixed and Boundary Lubrication

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A B S T R A C T

The article presents the results of a study of metal oleates for friction with mixed and boundary lubrication. The objects of study are copper (II), zinc (II), and tin (II) oleates. The boundary friction coefficient in a "steel - steel" friction pair was measured at an II5018 testing machine according to the "roller-block" scheme at different temperatures. The friction coefficient for mixed lubrication was measured in a plain bearing during the transition between hydrodynamic and boundary lubrication. Hersey-Stribeck curves were constructed for the journal bearing. The investigated additives have the most significant effect on the friction coefficient when introduced into the oil without other additives and less significant effect when introduced into the engine oil. The investigated metal oleates affect the conditions for the transition between hydrodynamic and boundary lubrication in a journal bearing. The results show that copper oleate reduces the contact friction coefficient by 7-15 % when added to engine oil. Zinc oleate has a similar effect and reduces the friction coefficient by 5.5-8.5 %. Tin oleate reduces the friction coefficient by 23.5-31 %.

1. INTRODUCTION

The problems of reducing friction and wear are still relevant at the present stage of industrial development. Mixed and boundary lubrication as subjects of tribology are still the least studied. This complicates the development of correct engineering methods for calculating friction units operating with boundary lubrication. The selection of various lubricant compositions is carried out mainly empirically. Lubricants and additives hide a significant amount of friction reduction. Oleates of some metals are part of many lubricant compositions [1-4]. These lubricating compositions can significantly reduce the friction coefficient and wear of machine parts. Copper oleate is most widely used as a component of so-called metal-plating additives for lubricants. The concentration of copper oleate is from 3 to 60 % of metal-plating additives (MPA). Metal-plating additives are special additives to lubricants and provide the formation of secondary structures on the friction surfaces. These structures consist of a metal-clad film and boundary layers of various substances and servovite films [5]. Powders of metals and alloys (copper, tin, zinc, aluminum, bronze, etc.), oxides, and salts of metals are used as MPA and improve tribotechnical characteristics of friction units. Metal-plating additives in lubricants allow us to realize the zero-wear effect in friction units. This effect is based on the phenomenon of the selective transfer. The phenomenon of selective transfer is widely described in the literature and many works are devoted to studies of the effect of MPA on the tribological characteristics of liquid and plastic lubricants in different friction units [6-10].

Prokopenko et al. [3] presented a metal-plating additive that contains 25 to 60 % by weight of monovalent copper oleate. This additive (at a concentration of 0.075 % by weight) reduces wear during run-in from 2 to 5 times. Dubinin and others [10] presented an additive with copper, magnesium, yttrium, and lanthanide oleates. This additive reduces the friction coefficient by 50 % in the steel-steel contact.

Belolyubskij, Lozovskij, and Afanas'ev [4] presented a lubricant containing copper powder, polytetrafluoroethylene, tributyl phosphate, a copper-containing additive, and a soap plastic lubricant. The copper-containing additive contained 60 % industrial oil, 20 % copper oleate, and 20 % oleic acid. The authors determined the threshold of resistance to scoring scuff and linear wear at the contact of spherical steel samples with the grease samples. They found that the introduction of tributyl phosphate and copper-containing additives into the plastic lubricant provides an increase in its service life and at the same time significantly increases the anti-wear and extreme pressure properties.

Kozarov and Onischuk [9] presented a review study MPA and lubricants. The authors presented the classification of metal-plating lubricants depending on the type of MPA. Metal or alloy powders, metal oxides, metal salts, complex metal compounds, metalloorganic compounds, and organic compounds are used as metal-plating additives to lubricants.

MPA [1] provides antifriction and extreme pressure properties of the lubricant due to the effect of fearlessness in the friction pairs (steel-steel, steel-cast iron, steel-bronze, etc.) as a result of the formation of a protective (servovite) metal-coating film on the surfaces of parts in places of actual contact with a thickness of 1-3 microns and autocompensation of wear of friction pairs [10].

Oleate is the basis of well-known additives such as Valena, Servovit [1], etc. [3]. The purpose of this study is to determine the effect of metal ion on the tribological characteristics of metal oleates similar to copper (II) oleate. We have paid particular attention to the study of the transition between hydrodynamic and boundary lubrication in the journal bearing using Hersey-Stribeck curves. These curves are the basis for analyzing the operating conditions of journal bearings and the most common way to determine the influence of various factors on the performance of journal bearings [21,22].

2. CHARACTERISTICS OF RESEARCH OBJECTS

The objects of study are copper (II), zinc (II), and tin (II) oleates. Salts of these metals were selected to clarify the role of such parameters of metal ion, as the active metal and the radius of the ion. With an equal degree of the metal oxidation, these parameters are crucial for the adsorption of oleate from the lubricant, metal recovery on the steel surface, and other tribochemical processes due to the presence of additives. Tin is between iron and copper in a series of metal stresses. Zinc (as opposed to copper and tin) is a more active metal than iron. The radius of the zinc ion (II) is almost equal to the size of the copper ion (II). The radius of the tin ion (II) is almost 2 times larger. Table 1 presents the properties of copper (II), zinc (II), and tin (II) oleates.

Table 1. Properties of copper (II), zinc (II), and tin (II) oleates.

Additive	Copper oleate	Zinc oleate	Tin oleate
Chemical formula	$Cu(C_{17}H_{33}COO)_2$	$Zn(C_{17}H_{33}COO)_2$	$Sn(C_{17}H_{33}COO)_2$
Molar mass	626.45 g/mol	628.29 g/mol	681.61 g/mol
Form	Amorphous, dark-green substance	White solid	Liquid, color depends on the original oleic acid
Melting point, ºC	20...35	70	- 5...+5
Solubility: **- in water** **- in hexane**	Insoluble Soluble	Insoluble Soluble	Insoluble Soluble

Transition metal oleates are obtained by the interaction of aqueous solutions of alkali metal oleates with sulfates or transition metal chlorides. This results in the formation of transition metal oleates insoluble in water and forming a separate phase. In the case of easily hydrolyzing metal salts, for example, Sn (II), the reaction of oleic acid with metal oxides in a non-aqueous medium is carried out [11].

3. EXPERIMENT AND RESULTS

Lubricant compositions were prepared with each additive sample. The mass concentration of the additive was 1 % in synthetic motor oil of viscosity class SAE 5W-40 (API SN/CF) and in industrial oil I40A. Industrial oil I40A is a purified oil without additives for industrial equipment. We investigated the effect of additives on the friction coefficient in the journal bearing by mixed lubrication. The test rig was assembled based on friction machine II5018 (Fig. 1).

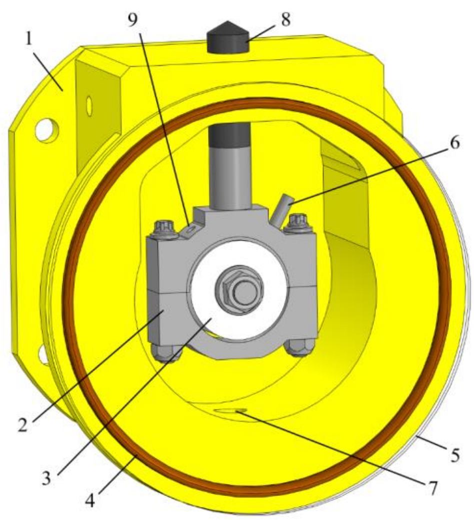

Fig. 1. The test rig for the journal bearing:
1 - modified friction chamber of the machine II5018; 2 - bearing housing with a coverage angle of 180 degrees; 3 - roller; 4 - sealing ring; 5 - protective glass; 6 - fitting for oil supply; 7 - hole for draining oil into the tank; 8 - loader; 9 - thermocouple installation site.

The load on the bearing varied from 500 to 5000 N. The oil supply pressure was 0.05 MPa. The shaft speed was 500 rpm. The temperature was fixed by a thermocouple on the outside of the bearing. The angle of coverage of the bearing was 180 degrees. The main parameters of the journal bearing are presented in table 2. Hersey-Stribeck curves are shown in Fig. 2. In Fig. 2 viscosity, angular velocity, and specific load are indicated as $\mu[mPa\cdot s]$, $\omega[1/s]$, $p[MPa]$, respectively.

Table 2. The main parameters of the journal bearing.

Parameter	Value
Diameter of the bearing [mm]	47.83
Length of the bearing [mm]	21.0
Radial clearances between the journals and the bearing [mm]	$25\cdot10^{-6}$
Anti-friction layer material	Aluminum and tin alloy

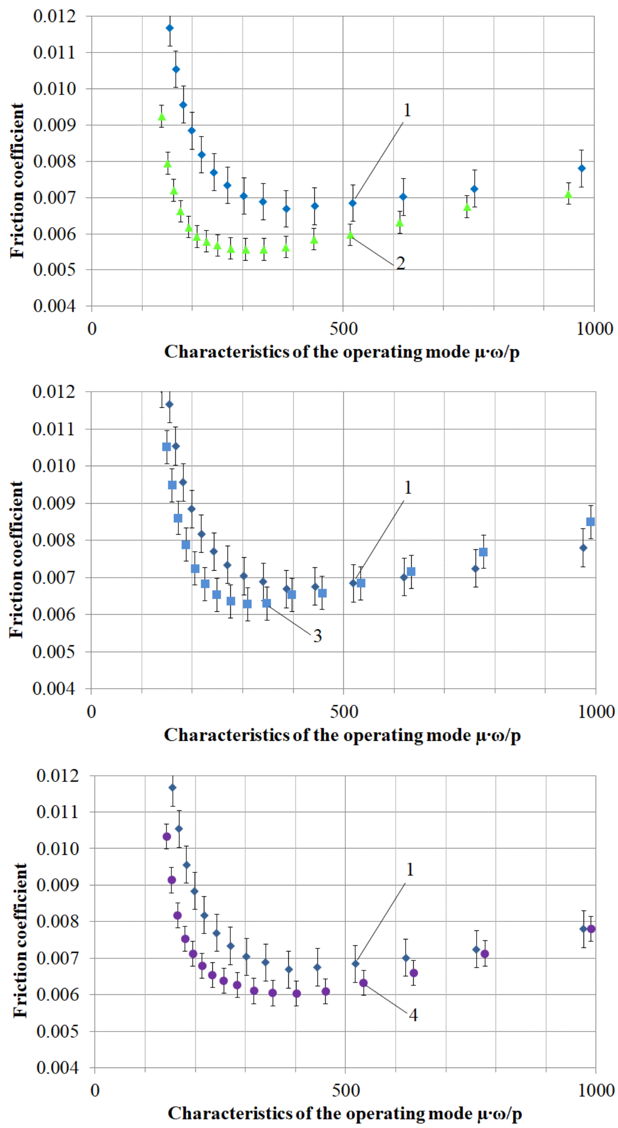

Fig. 2. Hersey-Stribeck curves for industrial oil:
1- Industrial oil I40A; 2 - Industrial oil I40A + 1% Copper (II) oleate; 3 - Industrial oil I40A + 1% Zinc (II) oleate; 4 - Industrial oil I40A + 1% Tin (II) oleate.

It was found that when the bearing is operated on oil with the addition of copper (II), zinc (II), and tin (II) oleates, the character of the Hersey-Stribeck curve changes in the region of the transition between hydrodynamic and boundary lubrication, that is, with mixed lubrication. The minimum friction coefficient reaches the values of 0.0062-0.0073 with the characteristic of the bearing operating mode (or Hersey number) in the region of 390-400 when lubricated with pure industrial oil I40A. The friction coefficient increases with a decrease in the Hersey number below 390, and when the Hersey number is 150, a transition to stable boundary lubrication occurs.

The minimum friction coefficient reaches values of 0.0055-0.0059 in the range of Hersey numbers 250-350 when copper oleate is added to the oil I40A. Thus, the region of transition between hydrodynamic and boundary lubrication expands significantly. The boundary friction coefficient is reduced by 30 %. A similar result is observed for lubricating compositions of I40A industrial oil with zinc and tin oleates. The boundary friction coefficient is reduced by 10-20 %.

The influence of metal oleates on the friction coefficient of boundary lubrication of the “steel 45 – steel 10” friction pair was investigated additionally on the machine friction II5018 according to the "roller-block" scheme (Fig. 3) at different temperatures. The sliding speed in the friction contact was 2.3 m/s. The temperature on the friction contact was controlled by a thermocouple installed in a partial liner at a distance of 5 mm from the working surface. The lubricant with the additive was fed into the friction zone by gravity at an average speed of 1 drop per 2 seconds.

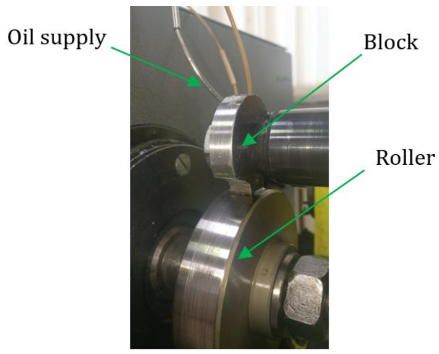

Fig. 3. Friction unit «roller-block» of the testing machine.

Each experience was repeated 3 to 6 times. The averaged results of measurement friction coefficient are presented in Figs. 4-6.

The results show that copper oleate reduces the friction coefficient in contact by 7-15 % when added to the engine oil. Zinc (II) oleate leads to a similar effect and reduces the friction coefficient by 5.5-8.5 %. Oleate of tin (II) leads to the decrease in the friction coefficient of 23.5-31 %.

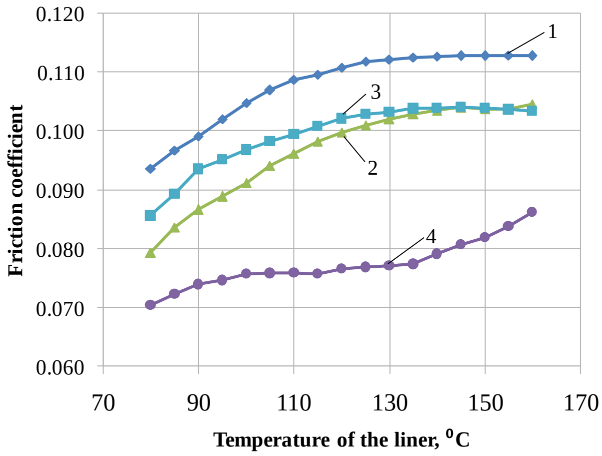

Fig. 4. Temperature dependence of the friction coefficient (unit load of 8 MPa) for motor oil: 1- Motor oil SAE 5W-40; 2 - Motor oil SAE 5W-40 + 1% Copper (II) oleate; 3 - Motor oil SAE 5W-40 + 1% Zinc (II) oleate; 4 - Motor oil SAE 5W-40 + 1% Tin (II) oleate.

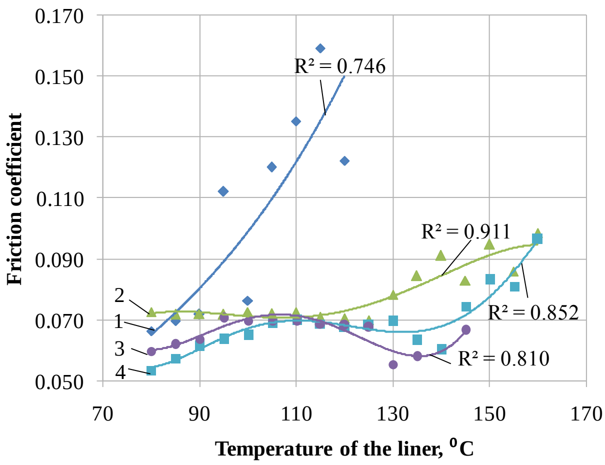

Fig. 5. Temperature dependence of the friction coefficient (unit load of 8 MPa) for industrial oil: 1- Industrial oil I40A; 2 - Industrial oil I40A + 1% Copper (II) oleate; 3 - Industrial oil I40A + 1% Zinc (II) oleate; 4 - Industrial oil I40A + 1% Tin (II) oleate.

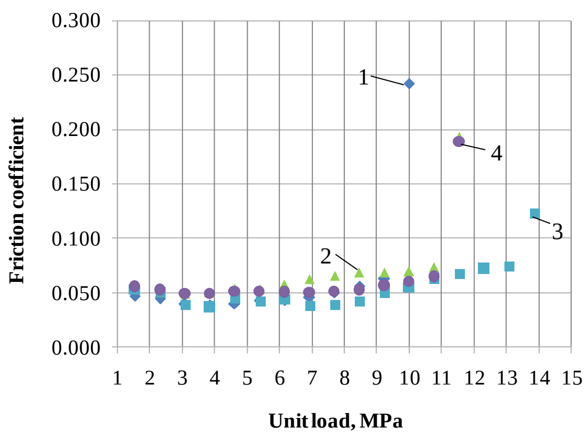

Fig. 6. Dependence of friction coefficient on unit load for industrial oil.

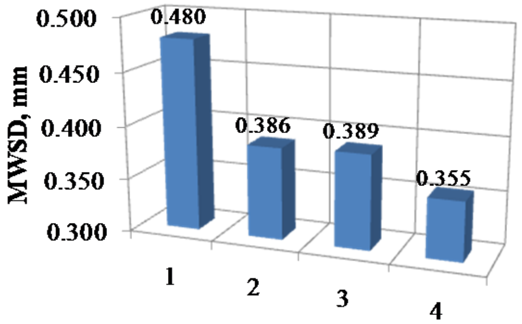

Fig. 7. MWSD (Motor oil SAE 5W-40).

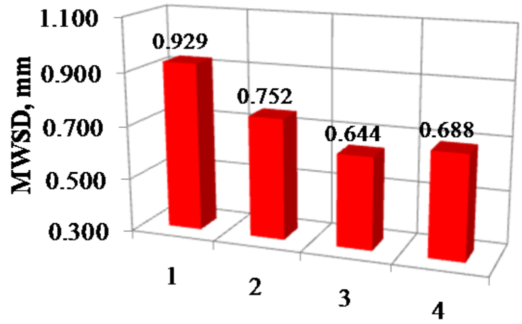

Fig. 8. MWSD (Industrial oil I40A).

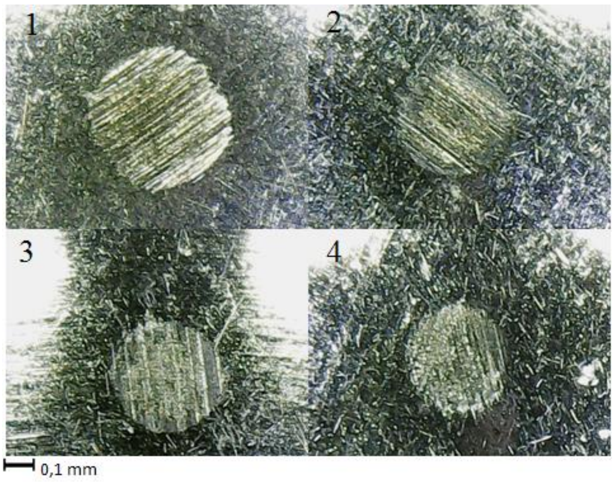

Fig. 9. The contact area of samples after the four-ball machine test (Motor oil SAE 5W-40).

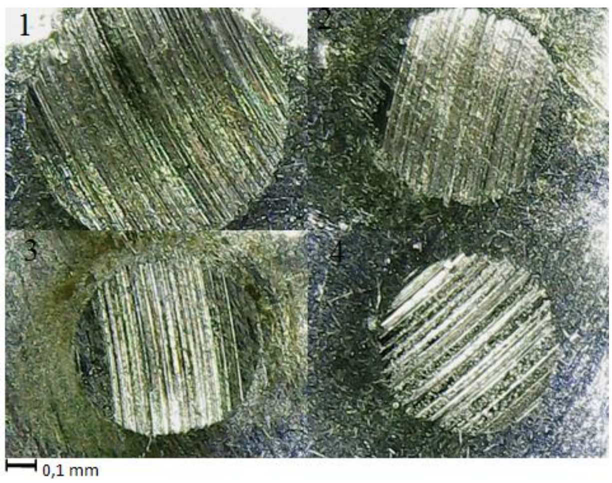

Fig. 10. The contact area of samples after the four-ball machine test (Industrial oil I40A).

The antiwear properties of lubricants were evaluated on the four-ball friction machine in accordance with GOST 9490-75. A four-ball friction machine is widely used for comparative evaluation of the antiwear properties of lubricants in many studies [12-16]. Figures 7 and 8 show the measurement results of the mean wear scar diameter (MWSD). All lubricants were tested at the load of 392 N. Contact areas of samples after the four-ball machine test are presented in Figs. 9 and 10.

4. CONCLUSION

The main conclusions drawn from this investigation are as follow:

1. The investigated additives have the most significant effect on the friction coefficient when introduced into the oil without other additives and less significantly effect when introduced into the engine oil. This is an obvious and expected result.
2. The investigated metal oleates affect the conditions for the transition between hydrodynamic and boundary lubrication in the journal bearing.
3. All investigated oleates slightly increase the friction coefficient at temperatures below 80 °C for both additive-free oil and motor oil. In the temperature range of 80...150 °C effect of zinc and copper oleates in the engine oil varies slightly.
4. Zinc is the more active metal than iron, and copper is the less active metal than iron. Tin in the electrochemical series of metal stresses occupies an intermediate position between zinc and copper. The absence of significant differences in the tribological properties of zinc and copper oleate in the "steel-steel" contact, as well as greater efficiency of tin oleate, indicate in favor of the adsorption mechanism of action of these additives. The contribution of tribochemical processes is insignificant. Also, this is confirmed by the fact that the sizes of the ions of bivalent copper and zinc are almost equal, and the size of the tin ion of bivalent is much larger. Consequently, the structure and dipole moment of tin oleate differ from the parameters of zinc (II) and copper (II) oleates.

5. Friction coefficients for all three additives converge with increasing temperature due to the processes of oleate dissociation. Thus, when the temperature increases, the effect of oleic acid on the friction process increases.
6. The dependence of the friction coefficients on the contact pressure confirms the assumption about the adsorption mechanism of oleate action. The highest contact pressure at which friction enters the boundary regime is observed for the most stable zinc (II) oleate (see Fig. 3).
7. The oil-soluble salts of the same metals with other organic acids, including a more complex structure, are of interest for further research. Since the tribological properties of the studied oleates are determined by adsorption processes, and at high temperatures are determined by the properties of oleic acid.
8. The results of anti-wear tests showed that all three oleates lead to almost the same decrease in wear. The wear spot diameter is reduced by 20...30 % by adding tin, zinc, and copper oleates to the motor and industrial oil. A comparison of the wear test results with the friction test results shows that the results of the four-ball machine tests were as close as those of the high-temperature tests. This may be since the secondary adsorption structures due to the adsorption of oleates on the metal surface are destroyed at high contact pressures and shear stresses. These structures at moderate contact pressures and temperatures cause a difference in the antifriction properties of the additives.

Adsorption of degradation products of additives (oleic acid) plays a major role at high shear stresses, as well as at high temperatures. The influence of the metal ion parameters on the structure of the adsorbed layer is minimal.

The results can be useful in the design of journal bearings [17,18]. Tests on other friction machines are of practical interest [19,20].

Acknowledgement

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