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TRIBOTECHNICAL PROPERTIES OF MOTOR AND INDUSTRIAL OILS WITH COPPER, TIN AND ZINC OLEATES

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Abstract: *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 which is the basis of well-known additives such as Valena, Servovit etc. The objects of study are copper (II), zinc (II) and tin (II) oleates. Salts of these metals are selected to clarify the role of such parameters of metal ion, as the active metal and the radius of the ion. 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. The influence of metal oleates on the friction coefficient of the friction pair of steel 45-steel 10 was investigated. The friction coefficient was measured on the machine friction II5018 according to the scheme "roller-pad" at different temperatures. The investigated additives have the most significant effect on the coefficient of friction when introduced into the oil without additives and less significantly when introduced into the engine oil. The results show that copper oleate reduces the coefficient of friction in contact by 7% -15% when added to the engine oil. Zinc oleate leads to a similar effect and reduces the coefficient of friction by 5.5% -8.5%. Oleate of tin leads to a decrease in the friction coefficient of 23.5%-31%.*

Keywords: *motor oil, industrial oil, metal oleates.*

1. INTRODUCTION

Reducing energy losses and wear in friction units of machines and mechanisms is an important task. A significant reserve to reduce friction is hidden in lubricants and additives. Oleates of some metals are part of many lubricant compositions [1-12]. These lubricating compositions can significantly reduce the coefficient of friction 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 surfing films [13]. 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 [14]. Metal-plating additives in lubricants allow to realize the zero-wear effect in friction units. This effect is based on the phenomenon of selective transfer [13]. The phenomenon of selective transfer is widely described in the literature and many works are devoted to studies of the effect of metal-plating additives on the tribological characteristics of liquid and plastic lubricants in different friction units [15-20].

Prokopenko et al. [8] 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 steel-steel contact.

Belolyubskij, Lozovskij and Afanas'ev [11] 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 and linear wear at the contact of a spherical steel samples with plasma 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 [19] 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, 12] provides antifriction and extreme pressure properties of the lubricant due to the effect of wearlessness 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 [20].

Oleate is the basis of well-known additives such as Valena [12], Servovit [1], etc. [2, 11]. 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.

2. CHARACTERISTICS OF RESEARCH OBJECTS

The objects of study are copper (II), zinc (II) and tin (II) oleates. Salts of these metals are 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 oxidation of the metal, these parameters are crucial for the adsorption of oleate from the lubricant, metal recovery on the surface of steel 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 [21]. 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 [21, 22].

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 [23]. Industrial oil I40A is a purified oil without additives for industrial equipment.

The influence of metal oleates on the friction coefficient of the friction pair of steel 45-steel 10 was investigated. The friction coefficient was measured on the machine friction II5018 according to the scheme "roller-pad" 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.

Each experience was repeated from 3 to 6 times. The averaged results of friction coefficient measurement are presented in figures 1-3.

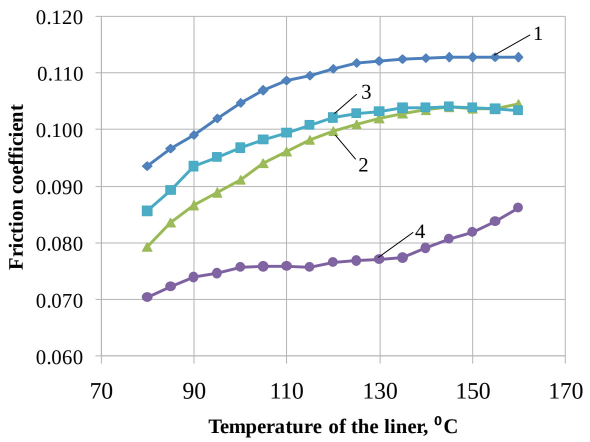

Figure 1. Temperature dependence of the friction coefficient (unit load of 8 MPa) for motor oil: 1- Motor oil SAE 5W-40; 2 - Motor oil SAE 5W-40 + 1% Copper oleate; 3 - Motor oil SAE 5W-40 + 1% Zinc oleate; 4 - Motor oil SAE 5W-40 + 1% Tin oleate

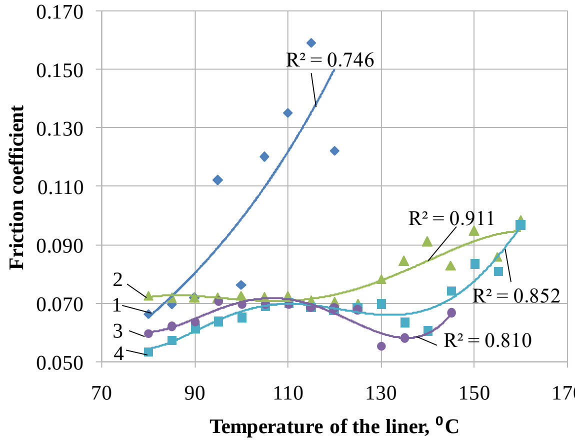

Figure 2. Temperature dependence of the friction coefficient (unit load of 8 MPa) for industrial oil: 1- Industrial oil I40A; 2 - Industrial oil I40A + 1% Copper oleate; 3 - Industrial oil I40A + 1% Zinc oleate; 4 - Industrial oil I40A + 1% Tin oleate

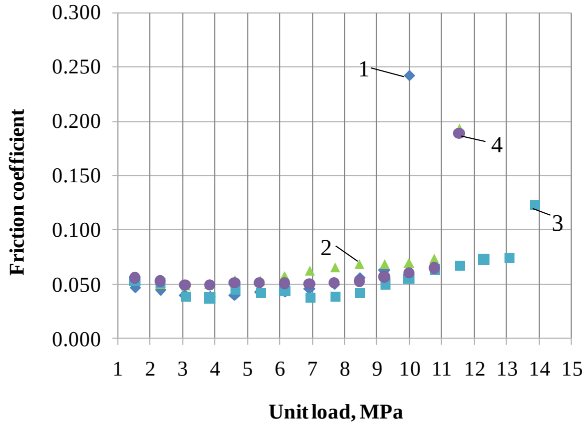

Figure 3. Dependence of friction coefficient on unit load for industrial oil

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

The effect takes place in industrial oil. In this case, the temperature range of the industrial oil becomes significantly greater. Oil without additives leads to a sharp increase in the coefficient of friction in the contact of friction at a temperature above 95 degrees. In addition, copper, zinc and tin oleate increase the load at which the transition to the boundary mode of friction occurs.

Antiwear properties of lubricants were evaluated on the four-ball friction machine in accordance with GOST 9490-75. Figures 4, 5 show the measurement results of the mean wear scar diameter (MWSD). All lubricants were tested at a load of 392 N. Contact areas of samples after four-ball machine test are presented in figures 6 and 7.

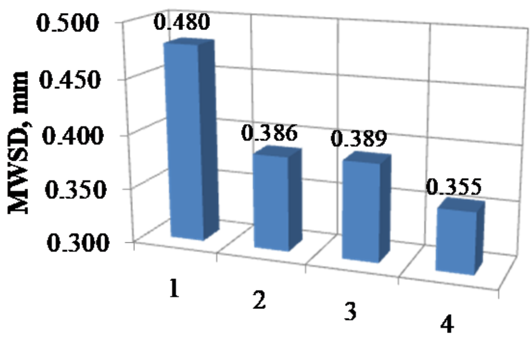

Figure 4. Mean wear scar diameter (Motor oil SAE 5W-40)

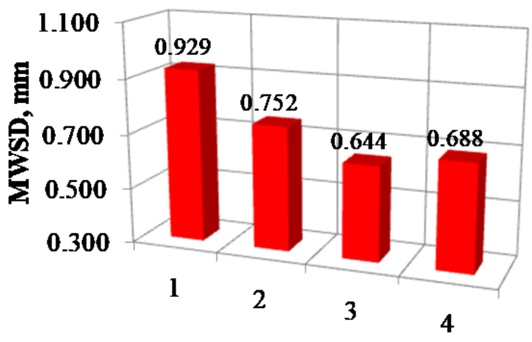

Figure 5. Mean wear scar diameter (Industrial oil I40A)

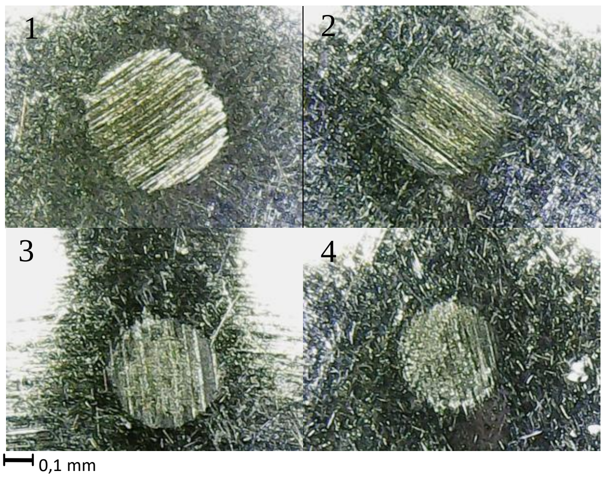

Figure 6. Contact area of samples after four-ball machine test (Motor oil SAE 5W-40)

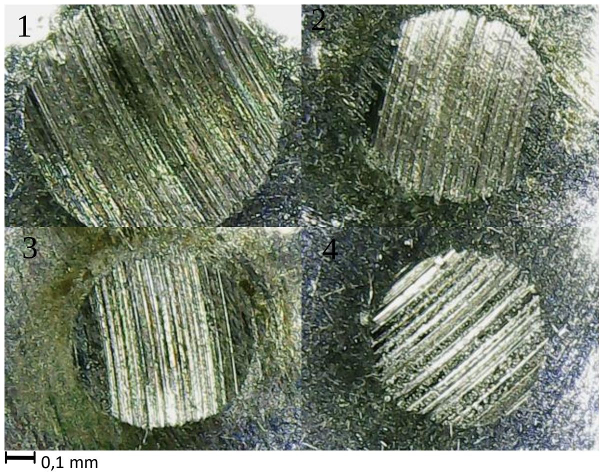

Figure 7. Contact area of samples after four-ball machine test (Industrial oil I40A)

4. CONCLUSION

The main conclusions drawn from this investigation are as follow:

1. The investigated additives have the most significant effect on the coefficient of friction when introduced into the oil without additives and less significantly when introduced into the engine oil. This is an obvious and expected result.
2. Tin oleate has the best anti-friction properties in both cases.
3. All investigated oleates slightly increase the coefficient of friction at temperatures below 80 ℃ for both additive-free oil and motor oil. In the temperature range of 80...150 ℃ effect of zinc and copper oleates in the engine oil varies slightly.
4. Zinc is a more active metal than iron, and copper is a 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 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. In addition, 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 differs from the parameters of zinc and copper 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 oleate (see Fig. 3). Thus, anti-friction properties are manifested while maintaining the structure of oleates.
7. For further research are of interest oil-soluble salts of the same metals with other organic acids, including more complex structure. 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 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 due to the fact that 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.

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REFERENCES

[1] V.G. Babel', D.N. Garkunov: Metal-coating multifunctional composition for motor, transmission and industrial oil, RU Patent 2,398,010, 6 Mar 2009. (on Russian)

[2] V.N. Bystrov, M.E. Stavrovskij, E.A. Lukashev: Metall-plaguing additive for lubricating compositions, RU Patent 2,293,758, 11 July 2005. (on Russian)

[3] S.V. Inshakov, V.I. Balabanov, S.A. Ishchenko, J.D. Kleptsova: Metal-coating additive for lubricant materials. RU Patent 2,503,713, 27 Nov 2012. (on Russian)

[4] V.I. Balabanov, V.J. Bolgov, S.A. Ishcenko, V.V. Lekhter: Metal plating restoration additive to plastic lubricating materials. RU Patent 2,432,386, 27 October 2011. (on Russian)

[5] V.N. Antonov, V.I. Balabanov, V.N. Bystrov: Metall-plaguing additive for lubricating compositions. RU Patent 2,044,761, 27 Sept 1995. (on Russian)

[6] V.I. Balabanov, S.A. Ishchenko, A.G. Gamidov: Metall-plaguing additive for lubricant materials. RU Patent 2,344,165, 20 Jan 2009. (on Russian)

[7] V.N. Bystrov, V.N. Antonov, Y.V. Lopatiyk: Metall-plaguing additive for lubricating compositions. RU Patent 2,186,834, 10 August 2002. (on Russian)

[8] A.K. Prokopenko, Y.S. Simakov, D.N. Garkunov, S.G. Krasikov: Metall-plaguing additive. SU Patent 859425, 30 August 1981. (on Russian)

[9] E.N. Sheveleva, Y.G. Savinyh, V.V. Harlamov, G.V. Bujskih, E.V. Kurdina: Metall-plaguing

additive for lubricating oils. SU Patent 1785263, 10 Jun 1999. (on Russian)
[10] E.L. Dubinin, V.V. Zaborskich, E.S. Koniychov: Metall-plaguing additive for lubricating oils. SU Patent 1721077, 23 Mar 1992. (on Russian)
[11] I.A. Belolyubskij, V.N. Lozovskij, V.A. Afanas'ev: Metall-plaguing lubricant. RU Patent 2000314, 7 Sept 1993. (on Russian)
[12] V. Babel, D. Garkunov, S. Mamikin, P. Kornik: Metal-containing oil-soluble composition for lubricant materials. RU Patent 2,277,579, 26 May 2005. (on Russian)
[13] D.N. Garkunov, I.V. Kragelskij, A.A. Polyakov: Izbiratel'nyj perenos v uzlah treniya (Selective transfer in friction units). Transport, Moscow, 1969. (on Russian)
[14] A.S. Kuzharov, N.Y. Onishchuk: Svojstva i primenenie metalloplakiruyushchih smazok (Properties and application of metal-plating lubricants). CNIITEHKHIM, Moscow, 1985. (on Russian)
[15] D.N. Garkunov: Tribotekhnika (iznos i bezyznosnost') (Tribotechnology (Wear and Non-wear)). Moscow, 2001. (on Russian)
[16] G.P. SHpen'kov: O yavlenii izbiratel'nogo perenosa. Dolgovechnost' trushchihsya detalej mashin. Vypusk 4 (On the phenomenon of selective transfer. The durability of friction parts of machines. Issue 4). Engineering, Moscow, p 3–11, 1990. (on Russian)
[17] A. Firkovskij, G. Pol'cer: Strukturirovanie tribologicheskoj sistemy v usloviyah izbiratel'nogo perenosa. Dolgovechnost' trushchihsya detalej mashin. Vypusk 4 (Structuring of tribological system under conditions of selective transfer. The durability of friction parts of machines. Issue 4). Engineering, Moscow, p 15–29, 1990. (on Russian)
[18] V.N. Bystrov: EHffekt bezyznosnosti i ego primenenie v tekhnike. Dolgovechnost' trushchihsya detalej mashin. Vypusk 5 (The effect of wearlessness and its use in technology. The durability of friction parts of machines. Issue 5). Engineering, Moscow, p 3–22, 1990. (on Russian)
[19] A.S. Kuzharov, N.Y. Onishchuk: Metalloplakiruyushchie smazochnye materialy. Dolgovechnost' trushchihsya detalej mashin. Vypusk 3 (Metal-plating lubricants. The durability of friction parts of machines. Issue 3). Engineering, Moscow, p 96–143, 1988. (on Russian)
[20] Kandeva M, Kalitchin ZH, Tribological investigations of tribosystems during lubrication using vegetable oils and mineral-vegetable oil composites containing metal-plating additive. Part I: Friction. Journal of Environmental Protection and Ecology 19: pp. 785–802, 2018.
[21] I.L. Knunyanc: Himicheskij ehnciklopedicheskij slovar' (Chemical encyclopaedic dictionary). Sovetskaya ehnciklopediya, Moscow, 1983. (on Russian)
[22] CRC Handbook of Chemistry and Physics. — 89th Edition. — Taylor and Francis Group, LLC, 2008-2009.
[23] GOST 20799-88 Industrial Oils. Technical conditions, 1988. (on Russian)