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Biomimetic Approach to the Design of Antiwear Additives To Eco-Friendly Lubricating Compositions

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It has been shown by standard test methods for a number of 1,3-dicarbonylic copper (II) complexes as an example that biomimetic approach can be used in the molecular design of antiwear additives for eco-friendly lubricating compositions. The effect of the structure of alkyl substituents of the chelate unit of complexes on the thickness of the antiwear layers of the friction zone has been established by Auger electron spectroscopic studies.

Keywords: Antiwear additives; Coordination compounds; Tribology; Auger electron spectroscopy (AES).

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Introduction

The lubrication industry uses a variety of terms to address “environmental” lubricants. “Environmentally acceptable” (EA) lubricant is the most commonly used term, which is reflected in the ASTM D 5864-95 standard. A number of commercially available lubricating oils, greases, hydraulic fluids based on vegetable oils, synthetic esters, polyglycols comply with the criteria of the above standard, viz: 60 % biodegradability into CO₂ and water within 28 days [1]. However, since February 2005 after the implementation of the Kyoto Protocol, only the lubricating compositions whose base fluids are manufactured using renewable raw materials and which contain appropriate additives can be positively classed as eco-friendly lubricants. The fats of plants and microalgae and their synthetic derivatives (esters of fatty acids and aliphatic alcohols or polyols) as base fluids for lubricants [2, 3] fully comply with the present-day requirements.

It was found in semiempirical way that of the large variety of antiwear additives to lubricants based on mineral and synthetic oils, coordination compounds of transition metals and various polydentate organic ligands, such as phosphorus-, sulfur- containing ones, are some of the most efficient additives [4]. However, these ligands are classified as environmentally dangerous substances [5]; besides, the sulfur- containing additives are “poisons” for copper- containing friction pairs, such as bronze/steel, since these additives cause increased wear [6]. Basing themselves upon their experience in the development of lubricants and lubrication systems for a multitude of machines and facilities, the experts of the U.S. Army Corps of Engineers (USACE) came

definitively to the conclusion that it is necessary to develop new types of additives oriented towards use in really eco-friendly, biobased lubricating compositions [1]. An example of the implementation of this world trend is development of environmentally friendly lubricants for the sheet metal forming operations [7].

I. Experimental

Ethyl laurate was synthesized by esterification of lauric acid with ethanol from readily available raw materials of vegetable origin according to known method [8]. After repeated fractional distillation (bp 92°C, 12 Pa), the compound had an acceptable purity, 99.7 % (GC/MS Agilent 6890/5973 inert). Four-ball wear test machine (Falex) and SRV test machine (Optimol) were used for tribology research. The Auger electron spectroscopic (AES) analyses were performed in the ultra-high vacuum chamber (approx. 10⁻⁸ Pa) of a JEOL JAMP-10S scanning microprobe. The accelerating voltage of the primary electron beam and the beam current were 5 kV and 1 μA, respectively. The diameter of the beam was 0.5 μm. The spectra were recorded with a cylindrical mirror analyser in the derivative mode, $E \cdot dN(E)/dE$ (where $N(E)$ is the number of electrons with energy E) vs. the kinetic energy, E . The energy resolution, $\Delta E/E$, of the analyser was ~ 0.7 %. The depth profiles were obtained using argon ions to sputter sequential atomic layers with an accelerating voltage of 2 kV. The sputtering rate was 1 nm/min. For the AES analyses, the most wear-resistant portions of friction surfaces, i.e. portions on micro-asperity tips of wear tracks, were selected. A detailed description of the technique of AES experiment for above purposes is

given in [9].

II. Results and discussion

Lauric acid ethyl ester was selected as the simplest representative of the environmentally acceptable base fluids for the lubricating compositions. The compound is nontoxic and has a wide temperature range of liquid state. Ethyl laurate is one of the base oils that are most resistant to thermal oxidative degradation, which minimizes the effect of autoxidation on the tribological characteristics of lubricating composition [6]. To satisfy the environmental challenges to the full, a biomimetic approach was employed to select chemical structures of the model additives being developed by us, viz. the central atom (copper) of these coordination compounds is one of the metals in the series of the indispensable elements (Mg, Ca, Fe, Cu, Zn, etc) of the biochemical systems of living organisms [10]. The organic constituents (ligands, L) of the above complexes are derivatives of β -dicarbonyls, compounds that occur in Nature [11]. It should be noted that β -ketoesters are patented as lubricant additives [12]. An effective synthetic method for β -ketoesters, including hexyl acetoacetate has been developed [13]. We had investigated earlier a number of copper (II) complexes of the general formula CuL_2 (**1-4**), where HL (proligands) is: **1** 2,2,6,6-tetramethyl-3,5-heptanedione; **2** 2,4-decanedione; **3** hexyl acetoacetate; **4** *tert*-butyl acetoacetate. It has been found by spectroscopic studies that compounds **1-4** are isostructural both as crystals and in solutions of nonpolar and weakly-polar solvents: they have a square-planar structure of the chelate unit [14], which is in good agreement with X-ray crystallographic data for the complexes **1** and **4** [15]. Ethyl laurate as a base fluid as well as lubricating compositions **1-4**, solutions of copper complexes (0.07 mol/L), were tested for antiwear and antifriction properties in accordance with the requirements of the ASTM D 4172-94 standard (Four-Ball Method) at a load of 392 N (40 kgf). The results of the tests showed that though the base fluid has a low viscosity ($2.63 \text{ mm}^2/\text{s}$ at 40°C) [15], it possessed good tribological characteristics: wear scar diameter $D_s = 0.53 \text{ mm}$, average friction coefficient $f_{av} = 0.049$. The wear scar diameter in the lubricating compositions turned out to be of the same order of magnitude as in ethyl laurate. For the scientists to deal with the problems of friction and wear, an important point at all considerations is the question of whether a protective layer is formed or, alternatively, the bulk material is modified. Scherge et al. had ascertained definitely by several instrumental methods, including AES: the depth profiles have proved that foreign chemical elements can be detected up to depths of several hundred nanometers in the volume. The depth of penetration of these elements correlates with microwaviness (wavelength and amplitude) of friction surfaces and also with macro effects such as change in friction coefficients and amounts of wear [17]. At the friction zone, an intensive mass transfer of chemical elements occurs from solid body into lubricating fluid and on the other hand – the atoms of the additive of the

lubricating composition can penetrate deeply under friction surface [18]. The surfaces and near-surface layers of wear tracks on steel balls were investigated by AES. It has been found by layer-by-layer Ar^+ ion-beam etching that the ultimate depth of penetration of copper atoms (65 nm for sample **1**, 11 nm for sample **2**) into metal matrix is affected by the structure of the alkyl substituents of ligands rather than by chemical structure of the nearest environment of the central atom of complexes. It was a surprise to us that bis(2,2,6,6-tetramethyl-3,5-heptanedionato)copper (II), $\text{Cu}(\text{DPM})_2$, which has a much better screening of the central atom by branched alkyl substituents in comparison with bis(2,4-decanedionato)copper (II), $\text{Cu}(\text{AHM})_2$, which has linear alkyl substituents, may give such an effect when using it as an additive. As was pointed out above, however, these complexes have a planar structure of the chelate unit. This is a consequence of copper atom d-orbital being involved in the aggregate π -electron system, which encompasses both chelate rings, together with the metal atom, which stabilizes the overall planar double-cyclic structure of the chelate skeleton (fig. 1).

In the complex $\text{Cu}(\text{DPM})_2$, the central atom has nine

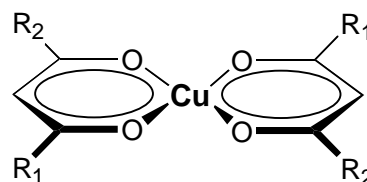


Fig. 1. Structure of the copper complexes **1** ($R_1 = R_2$ – *tert*-butyl) and **2** (R_1 – methyl, R_2 – hexyl).

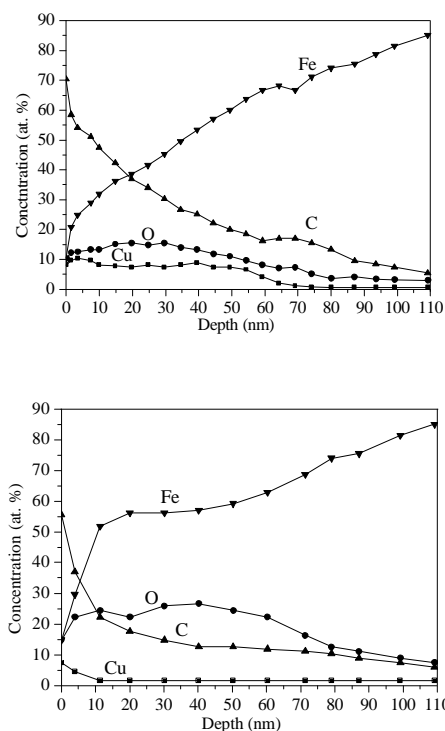


Fig. 2. Depth profile by Auger electron spectroscopy of wear tracks. Upper graph: sample **1**; lower graph: sample **2**.

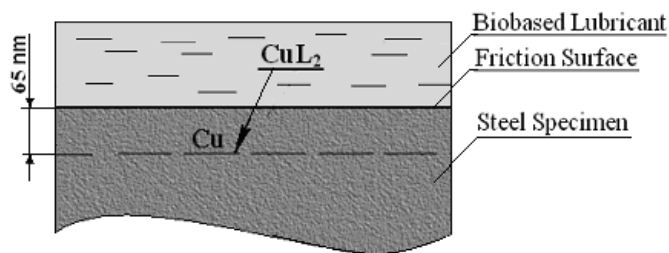


Fig. 3. Dzyuba. Penetration of copper atoms under the friction surface.

Table 1.

Antiwear and antifricition properties of base fluid and the lubricating composition 1-4 (ASTM D 6425-99).

Sample #	D_s , mm	f_{min}/f_{max}	f_{15}	f_{30}	f_{90}	f_{120}
Ethyl laurate	1.46	0.105/0.153	0.133	0.114	0.130	0.138
1	0.98	0.120/0.155	0.125	0.123	0.121	0.120
2	0.99	0.119/0.153	0.127	0.123	0.121	0.119
3	1.05	0.110/0.137	0.122	0.121	0.112	0.111
4	1.05	0.127/0.138	0.130	0.135	0.135	0.138

d-electrons and acts as an acceptor, completing the construction of its d-shell to the stable $3d^{10}$ configuration, whereby it makes for the intensification of donor properties of alkyl substituents of the ligand [19]. The different depth of penetration of copper atoms under the friction surface of samples 1 and 2 may be attributed to a difference in the electron donating ability of the substituents ($t\text{-Bu} > \text{Hex} > \text{Me}$) of the chelate rings of the complexes $\text{Cu}(\text{DPM})_2$ and $\text{Cu}(\text{AHM})_2$ (fig. 2).

The AES investigations were carried out under the conditions of sample evacuation to 10^{-8} Pa. The complex $\text{Cu}(\text{DPM})_2$ is a light-volatile compound [18], therefore the presence of this substance in the native form on the friction surface under ultra-high vacuum conditions is ruled out. The copper atoms, detected by the above method, on the friction track and all the more so, under the friction surface of sample 1 may be interpreted as a product of chemical interaction between the additive and the body of steel specimen (fig. 3).

Very probably, the excellent lubricity of the base fluid masks the action of additives in compositions 1-4 in the case of testing by the ASTM D 4172-94 method. Therefore, we used the ASTM D 6425-99 method, where testing is performed at much larger specific loads on the friction assembly than in the Four-Ball Method. The

results of tests at a load of 300 N are listed in the table 1.

Conclusions

Comparative analysis of the data listed in the table shows that the additives improve considerably both the antiwear and antifricition characteristics of the base fluid and gives an option for further development of eco-friendly commercially available lubricants. The work is in progress, and we hope that the approach described in this communication will be common to a number of other coordination compounds as additives, complexes with various biometals as central atoms and other polydentate organic ligands, structural analogs of compounds occurring *in vivo*.

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В.І. Дзюба, Л.І. Коваль, О.Л. Ільницька, В.І. Пехньо

Біоміметичний підхід в дизайні протизношувальних присадок для екоприйнятних мастильних композицій

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На прикладі ряду 1,3-дикарбонільних комплексів міді (II), стандартними методами випробувань показано, що біоміметичний підхід може бути застосовано в молекулярному дизайні протизношувальних присадок для екоприйнятних мастильних композицій. Оже-спектральними дослідженнями виявлено вплив будови алкільних замісників хелатних циклів комплексів на товщину протизношувальних шарів зони тертя.