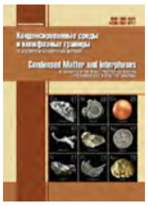

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Electrophilic-nucleophilic properties as a factor in the formation of antifriction and hydrophobic properties of surface-modified metals with ammonium and organosilicon compounds

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Abstract

Stabilisation of the functional properties of dispersed and compact metals, as well as the regulation of their reactivity, improvement of water-repellent, antifriction and anti-corrosion properties by creating the protective films on the surface is an urgent problem in relation to obtaining new materials. Previously, research conducted at REC "Nanotechnology" of the St. Petersburg Mining University proved that chemisorption of ethylhydridesiloxane vapours together with surfactants based on quaternary ammonium compounds has a beneficial effect on the water-repellent properties of metals. In order to obtain the physicochemical mechanism of the hydrophobisation of the surface of modified dispersed metals for the first time, the study of the electrophilic-nucleophilic properties of the active substances of the surface modifiers of metals was carried out using the methods of quantum-chemical modelling using HyperChem software package. The dipole moment, energy of the highest occupied and the lowest unoccupied molecular orbitals, electrophilic-nucleophilic properties were determined. The series of enhancement of nucleophilic/electrophilic properties and dipole moment for modifiers were obtained. The donor-acceptor properties, the differences in the characteristics of the molecules of alkamon, triamon, and hydrophobic silicone organic liquid were quantitatively and qualitatively established. The regularities of the formation of hydrophobic and antifriction properties in the composition of industrial oil I-20-surface-modified metal with various electrophilic-nucleophilic properties of the applied substances.

Keywords: Electrophilic-nucleophilic properties, Dispersed metals, Ethylhydridesiloxane oligomer, Quantum-chemical modelling, Hydrophobicity, Antifriction properties

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1. Introduction

Stabilisation of the functional properties of metals, both dispersed and compact, as well as the regulation of their reactivity, improvement of water-repellent, antifriction and anticorrosion properties by creating the thinnest protective films on the surface is an urgent problem in relation to creating new materials. One of the promising approaches to obtaining these materials is the method developed at the Saint Petersburg Mining University for the layering of molecules of different sizes on metals (RF patent No. 2425910), implemented at a number of enterprises of the mineral resource complex of the Russian Federation and the Republic of Belarus. As part of the research at REC "Nanotechnology" of the St. Petersburg Mining University, it was proved that the chemisorption of the oligomer vapours of ethylhydridesiloxane together with surfactants based on quaternary ammonium compounds (QACs) increases the water-repellent properties of metals, such as, for example, aluminium and copper [1-3]. In this study, dispersed copper powder of the PMS-1 (Cu) grade – GOST 4960-75 was used as a metal-substrate. Interest in copper powder is explained by the potential of practical application as additives to lubricating compositions for various purposes and components of heating elements [4–7].

Modern developments in physical chemistry, chemical technology, dedicated to improving the properties of oils and lubricants, contribute to the solution of the designated problems [8–10]. At the same time, many known additives and fillers are quite expensive and do not always meet the environmental safety requirements. The latest developments of the Saint Petersburg Mining University in the modification of dispersed metal surfaces with organic preparations based on quaternary ammonium compounds allowed achieving a significant antifriction effect when adding appropriate additives to lubricating compositions [4]. The performed studies, including those presented here, allowed not only to substantiate the significant antifriction, anti-corrosion, and water-repellent effects when adding additives to organic matrices of oils, greases, and paints, but also describe the chemical principles of the synthesis of surface-modified metals, including the justification of the reagents used in the synthesis, based on copper PMS-1. The corresponding technology is, in fact, an energy- and resource-saving synthesis technology, since the layering of ammonium compounds occurs at room temperature, and the amount of the applied modifier was not higher than 1 mass % of the sample. Monolayer application of the substance (5 mg/m^2) provides significant savings in material resources [1].

When studying the hydrophobic and antifriction properties of the surface of modified samples based on copper powder PMS-1, interesting effects were revealed when applying organic modifiers (ammonium compounds and ethylhydridesiloxane) in various combinations on the surface of dispersed copper [1, 2]. It was found that Cu/T/A, Cu/A/HSL, Cu/(A+T) samples treated with ethylhydridesiloxane (HSL), triamon (T), and alkamon (A) - preparations based on ammonium quaternary compounds were characterised by a significant increase in the water-repellent properties [1,2]. At the same time, treatment with only one modifier did not enhance the hydrophobicity of the sample surface. It is important to note that according to the literature, the deposition of three or more layers does not lead to a significant hydrophobic and antifriction effect due to the weak interaction of the layers with a solid substrate [1,3].

The purpose of this study was the investigation of antifriction properties of additives based on dispersed copper in the composition of the industrial oil I-20, the analysis of the electrophilic-nucleophilic properties of modifier molecules used for the production of films on dispersed metals, using quantum-chemical modelling methods for further physicochemical substantiation of the antifriction effect in the composition of lubricants and the effect of hydrophobization of the surface of modified dispersed metals.

2. Experimental

Stabilized copper powder, grade PMS-1 (GOST 4960-2009), was used as the initial dispersed metal. A modern approach to the production of thin films on the surface of dispersed and compact metals is the method of layering different-sized molecules of quaternary ammonium compounds used in this study, which has demonstrated to be a promising method for regulating various surface properties of dispersed metals such as copper, aluminium, nickel, etc. The surface modification of copper powders was carried out in alkamon (GOST 10106-75) and/or triamon (TU 6-14-1059-83) vapours based on QACs, as well as in vapours of a hydrophobic silicon-organic liquid HSL-94 based on ethylhydridesiloxane at room temperature, vapour pressure of 0.7–1.0 MPa [1–4]. The possibility of a synergistic enhancement of the water-repelling properties during the adsorption of QACs and ethylhydridesiloxane molecules on the surface is of particular interest [1]. The composition of triamon (T) - tris- (-oxyethyl) methyl-ammonium-methyl sulphate (TOMAM) – in pairs corresponds to the chemical formula $[(HOC_2H_4)_3N^+CH_3][CH_3SO_3^-]$ with low molecular weight radicals at the nitrogen atom. The composition of the cation of the used alkamon (A) contains a significant C_{17} hydrocarbon radical. The structural formula of the active substance of the used alkamon: $[C_nH_{2n+1}OCH_2N^+(CH_3)(C_2H_5)_2][CH_3SO_4^-]$, where $n = 16$. HSL-94 is hydrophobic silicon-organic liquid based on organohydridesiloxanes; it is an oligomer of polyethylhydridesiloxane [11]. HSL is used as a reagent for the enhancement of the water-repellent properties of textile, leather and paper products, as well as products made of concrete, brick, and other building materials. Usually it is applied from solutions [11]. It is widely used as an industrial surface water repellent in construction. The following samples were studied depending on the sequence and chemisorption mode of QACs and HSL preparation on the surface of the initial copper powder (Cu): Cu/(A+T), Cu/A, Cu/HSL, Cu/T/A, Cu/A/T, Cu/T/HSL, Cu/A/HSL, and Cu/T. A sample of Cu/(A+T) was obtained in a mixture of A and T vapours (1:1), Cu/T/A was obtained by sequential deposition of T and A.

Water-repelling properties (hydrophobicity) were evaluated by the adsorption of water vapour on the surface of the samples by the gravimetric method. The relative pressure of water vapour was about 0.98 ($P_{H_2O}/P_S \to 1$, where P_S is the saturated H_2O vapour pressure). The fact of water vapour adsorption by the samples was additionally monitored by the appearance in the XPS spectra and an increase in the intensity of the peak with a binding energy of 532.5±0.1 eV, which is characteristic for water adsorbed on the metal.

Quantum-chemical modelling was carried out using the HyperChem software package according to the semiempirical MNDO method. The application method and the fundamental principles of the calculation method are described in the literature [12–16]. Quantum-chemical calculations were based on the solution of the Schrödinger equation [17]. Direct calculation of multielectron atoms and polyatomic systems seems to be a non-trivial task due to the significant amount of required computational time. For this reason, semiempirical (approximate) methods for solving this equation are gaining importance in quantum chemistry [16–18]. According to the degree of approximation, all quantum chemical methods are divided into nonobservational (*ab initio*), semi-empirical, empirical (a group of methods of molecular mechanics) and methods of molecular dynamics [17, 19].

HyperChem is a software product providing opportunities for the quantum mechanical modelling of atomic and molecular structures. It includes programs, implementing the methods of molecular mechanics, quantum chemistry, and molecular dynamics. Force fields of molecular mechanics that can be used in HyperChem are MM+, Amber, OPLS, and BIO+ (based on CHARMM).

To determine the fundamental tribological characteristics: friction force (*F*fr) and coefficient of friction (*f*) of tribosystems industrial oil I-20 (GOST 20799-88) with the addition of dispersed surface-modified metal (M = Cu, Al), a friction machine DM-29M was used. The friction pair of the DM-29M machine was slide bearing (Shaft – steel 45 (GOST 1050) – insert – bronze BrAZh 9-4 (GOST 18175), continuously lubricated with I-20 oil with adsorption-modified metal powders (Cu). The concentration of the additive in the composition of the oil did not exceed 1 wt. %. In addition, the integral index of friction *D* proportional to the friction force, was monitored by the acoustic emission method using a certified device ARP-11 (pressure P = 47 MPa) [3.5] (Table 1).

3. Results and discussion

In this study, the friction force (F_{fr}) and coefficient of friction (f) for tribosystems (copper

Table 1. Comparison of the adsorption of water vapor (a, g/g) on a surface-modified metal (Cu) with the value of the integral friction index D (pressure P = 47 MPa) [1]. D for I-20 oil is 1500

Type of powder	but$_{H_2O}$, g/g	Integral friction index D for industrial oil with powder
Cu/A	0.0299	1300
Cu/T	0.0268	1100
Cu/T/A	0.0260	270
Cu	0.0445	1450
Cu/(A+T)	0.0310	1480

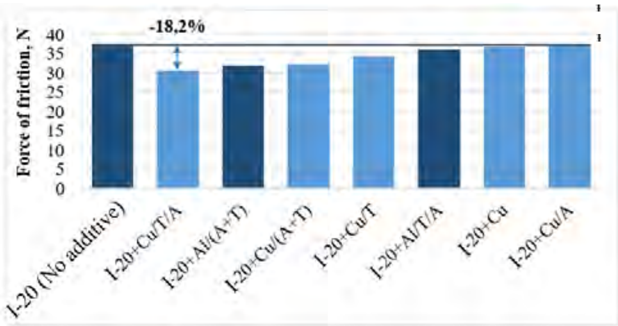

Fig. 1. The force friction in the tribosystem (load 5 kN) containing additives (1 wt%) based on dispersed copper, modified in various modes

powder-industrial oil I-20) were measured using a DM-29M friction machine for the first time. From the data shown in Fig. 1 and Table 2 it follows that the most significant decrease in the friction force and coefficient of friction in the slide bearing of the DM-29M friction machine lubricated with industrial oil I-20 was provided by copper powder (PMS-1) processed in the mixed mode (Cu/(A+T)) and sequential mode (Cu/T/A) with both modifiers (alkamon and triamon). It is interesting that the Cu/T/A and Cu/(A+T) samples were superior in terms of antifriction properties in the composition of lubricants when compared to the samples modified in A and T pairs and separately. This synergistic effect was manifested both by the assessment of antifriction properties based on the integral friction index D [1] and using the DM-29M friction machine (Table 1). According to data shown in Tables 1 and 2, there is a superiority in the ability to reduce friction of additives of the Cu/T/A type over additives treated with only one modifier, as well as over additives of a similar type Al/(A+T) and Al/T/A based on the dispersed aluminium (PAP-2) that was investigated earlier [1].

According to the developed concepts [1,4], when approaching the "dry friction" mode (load pressure ⩾ 40 MPa), the antifriction properties of the tribosystem were largely determined by the properties of the surface of the solid additive. Therefore, the reduction of friction in the system by several times (Table 1) at high pressures is quite understandable taking into account the difference in the surface of the additives in terms of hydrophobicity and adhesion of the applied surfactant film to the metal [3–5]. More modest indicators of the reduction of the friction force and coefficient of friction in the system with similar additives (Fig. 1, Tables 2, 3) were associated with the fact that the measurement of these characteristics using friction machine is technically possible at low pressures (not higher than 17 MPa). The enhancement of the antifriction effect is associated with an increase in the influence of the surface of the solid additive during the transition from the liquid-phase

Table 2. Characteristics of Cu-additives (1 wt%), including the relationship equation $F_{fr} = \mathcal{F}(N)$, change of $F_{fr}(\Delta F_{fr})$ relative to the initial industrial oil the value of the coefficient of friction (f)

No.	Additive	Equation $F_{fr} = \mathcal{F}(N)$	R^2	ΔF_{fr}(av.), %	ΔF_{fr}(N = 5 kN), %	f(N = 5 kN)
1	Al/(A+T) [1]	$y = 0.0370x + 12.47$	0.991	−11.41	−15.92	0.0075
2	Al/T/A [1]	$y = 0.0480x + 10.81$	0.992	−7.75	−3.69	0.0079
3	И-20 (no additive) [1]	$y = 0.0500x + 12.29$	0.994	0	0	0.0089
4	Cu/T/A	$y = 0.0375x + 12.02$	0.995	−13.79	−18.22	0.0063
5	Cu/(A+T)	$y = 0.0393x + 12.43$	0.994	−10.29	−14.39	0.0066
6	Cu/T	$y = 0.0395x + 14.69$	0.997	−9.04	−1.86	0.0072
7	Cu	$y = 0.0412x + 15.09$	0.991	+2.65	−2.17	0.0083
8	Cu/A	$y = 0.0418x + 15.90$	0.985	+6.46	−1.40	0.0091

Table 3. Dependence of the value of the coefficient of friction (*f*) on the loading pressure in the range of 50-500 kgf on friction machines DM-29M

No.	Additive	*f*, 50 kgf	*f*, 100 kgf	*f*, 150 kgf	*f*, 250 kgf	*f*, 500 kgf
1	Al/(A+T)	0.0299	0.0173	0.0125	0.0086	0.0064
2	Al/T/A	0.0275	0.0164	0.0127	0.0091	0.0074
3	И-20	0.0308	0.0185	0.0134	0.0098	0.0077
4	Cu/T/A	0.0281	0.0167	0.0118	0.0084	0.0063
5	Cu/(A+T)	0.0291	0.0173	0.0125	0.0088	0.0066
6	Cu/T	0.0339	0.0193	0.0139	0.0098	0.0069
7	Cu	0.0339	0.0205	0.0146	0.0103	0.0075
8	Cu/A	0.0372	0.0209	0.0146	0.0105	0.0077

friction mode to the boundary one, and further to "dry friction".

The need to study tribosystems in a wide range of loading pressures is explained by the widespread use of industrial petroleum oil in industry for lubricating a wide range of machine tool and mining equipment, characterized by uneven load on the actuating device.

The dependence between the friction force and the load for lubricating compositions with various Cu-additives based on I-20 industrial oil was approximated by a linear dependency with a confidence level R^2 in the range of 0.985 - 0.997. Cu-additives, which maximally reduce the friction force and coefficient of friction in the tribosystem (Cu/T/A, Cu/(A+T)), correspond to the equations with the minimum proportionality factor *k* (Table 2). The resulting equations $y = kx + b$ were similar to the formula for boundary friction ($F_{fr} = k(N + F_{af})$, where *k* is the coefficient of friction, *N* is the force of normal pressure (load), F_{af} is the additional force due to intermolecular attraction). F_{af} is minimal for Cu/T/A additive. Modification of copper allows adjusting the value of F_{af} (Table 2).

Water vapour adsorption isotherms for most copper-based samples correspond to type III isotherms [2] according to the classification of Brunauer, Deming and Teller [19-20]. From the data provided in earlier studies, taking into account the testing of samples in saturated water vapour for hundreds of hours, it follows that the most hydrophobic of the studied samples is a sample of the Cu/A/HSL type with sequentially chemisorbed alkamon and ethylhydridesiloxane [2].

As a result of analysing the data presented in Fig. 1 and Tables 1 and 2, the series of enhancement of antifriction and water-repellent properties for copper-containing additives were obtained:

I-20/Cu/T/A > I-20/Cu/T > I-20/Cu/A > I-20/Cu/(A+T) > I-20

← Decrease in D [1]

I-20/Cu/T/A > I-20/Cu/(A+T) > I-20/Cu/T > I-20 > I-20/Cu/A

← Decrease in Ffr (N = 5 kN)

Cu/T/A > Cu/T > Cu/A> Cu/(A+T) > Cu

← Increase in hydrophobicity [2]

As can be seen from the comparison of the series, the antifriction effect of copper additives in tribosystems increased as the hydrophobicity of the latter increased. However, application of a hydrophobic substance (A or T) to dispersed copper powder (PMS-1) did not allow achieving a high antifriction effect. The best antifriction properties were revealed for copper samples containing triamon in the surface layer with small (C_1–C_2) organic radicals at the nitrogen atom. This obviously contributes to the fact that the T molecules relatively easily fill the "gaps" of the factory stearic stabilizing film. Also, due to the steric accessibility of nitrogen atoms in triamon, favourable conditions for the metal-nitrogen

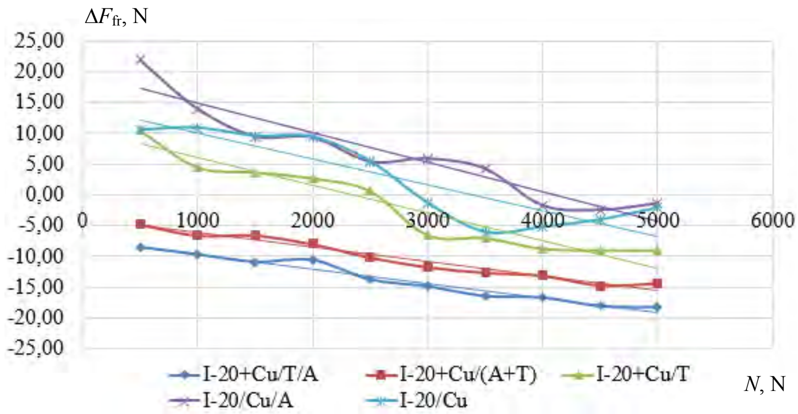

Fig. 2. Dependence of the antifriction effect in the tribosystem on the load for additives based on dispersed copper PMS-1, modified in different modes

interaction, enhancing the adhesion of the surfactant to the metal were created. The above is also evidenced by the tribological characteristics of the Cu/A sample treated with one alkamon, the addition of which to the oil composition did not lead to an increase in the antifriction properties in comparison with the addition of the initial PMS-1 copper powder (Table 2).

In this study, the quantum-chemical modelling using the HyperChem software package was applied for the determination of the structural-chemical and nucleophilic-electrophilic properties of molecules. The following molecular parameters were determined: dipole moment, distribution of electrostatic potential, energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The value of the dipole moment of the adsorbed molecule is important for the estimation of the change in the interfacial potential and the energy of interaction of the adsorbate with a solid surface [17, 21–23].

The dipole moment of the ethylhydridesiloxane oligomer corresponds to 3.02 D (Table 4), and its direction is shown by the dotted line in Fig. 3. Oxygen atoms (0.66 eV) of organic radicals were the most reactive in the case of

Table 4. Results of quantum chemical modelling of active component of HSL-94 and ammonium compounds

	HSL-94	Alkamon	TOM
Dipole moment [D]	3.0	20.2	5.3
Energy HOMO [eV]	2.37	−13.10	−6.21
Energy LUMO [eV]	10.10	−1.95	0.38
Molecular Excitation Potential ΔE [eV]	7.23	11.15	6.59
Electrophilic-Nucleophilic properties (donor-acceptor) properties	Nucleophile	Electrophile	Nucleophile

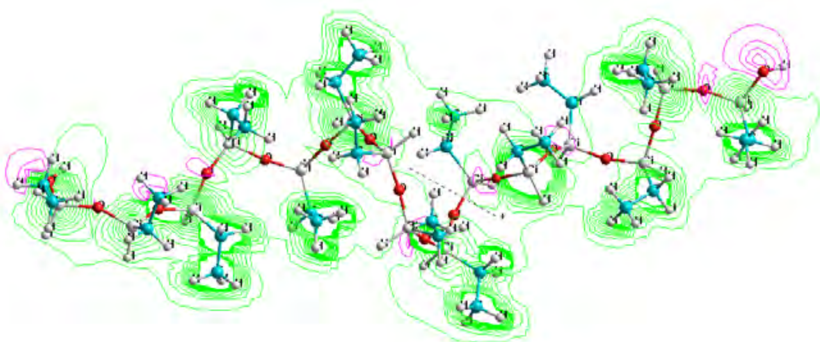

Fig. 3. Quantum chemical model of ethylhydridesiloxane oligomer (n = 15) with the distribution of electrostatic potential (silicon atoms – big grey balls)

electrostatic interaction (physical adsorption). For the determination of the nucleophilic and electrophilic (donor–acceptor) properties of the molecule, the energies of the lowest unoccupied and highest occupied molecular orbitals were determined, which were 2.374 and 10.097 eV, respectively (Fig. 4). Since the energy of LUMO is positive, the ethylhydridesiloxane oligomer molecule is a nucleophile. The excitation potential of the molecule was 7.233 eV. The results of a similar analysis of other molecules are shown in Table 4 for molecules of active substances in preparations based on quaternary ammonium compounds - triamon (TOMAM) and alkamon.

As can be seen from Table 5, samples containing combinations of modifiers with different nucleophilic-electrophilic properties (Cu/A/HSL), Cu/(A + T), Cu/T/A) in the surface layer possess the greatest hydrophobic and antifrictional effect, contributing to the chemical (electronic) interaction in the metal-deposited modifiers system, including interactions between deposited substances. Therefore, modification modes, including sequential treatment with hydrophobic compositions with different electrophilic properties, are most preferable for obtaining highly and superhydrophobic materials. It is interesting that modification with only one type of modifier (A, T, HSL) did not allow achieving a significant increase in the hydrophobicity of the surface in comparison with the original copper powder, probably due to the limited possibility of stabilizing the outer hydrophobic layer of the surface. The combination of electrophilic and nucleophilic modifiers allowing not only to block the hydrophilic centres of the surface, but also to increase the resistance of the metal-applied hydrophobic agents system to external influences.

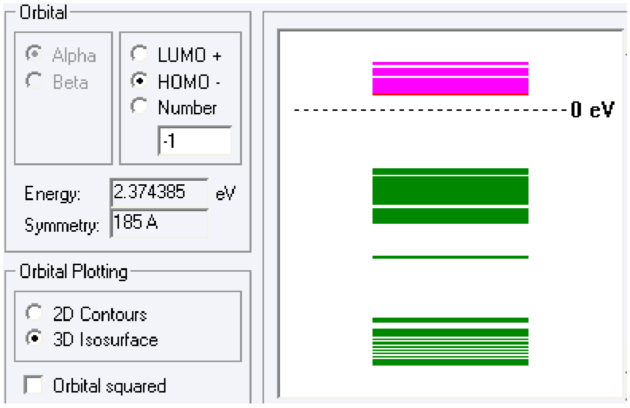

Fig. 4. The distribution of the molecular orbitals of ethylhydridesiloxane oligomer (HSL -94)

According to A. A. Abramzon, an increase in the adhesion of a surfactant film to a solid surface is the key to its successful hydrophobization and antifriction effect [24]. The possibility of donor-acceptor interactions metal - QACs, metal - silicon hydrides has been repeatedly proven by IR and XPS spectroscopy [1,25,26].

Conclusions

For the first time, fundamental tribological characteristics (force and coefficient of friction) were measured for copper-based samples in the composition of I-20 oil and compared with the hydrophobicity of additives and antifriction properties of systems with high loading pressures. Quantum-chemical modelling of reagent molecules used in the process of layering of different-sized molecules of quaternary ammonium compounds on metals was performed using HyperChem software package.

Table 5. Comparison of average values of water vapour sorption (P_{H_2O}/P_S = 0.98 ± 0.02) and friction force change for different samples in the time interval 24 ⩽ t ⩽ 216 h with electrophilic-nucleophilic (donor-acceptor) properties of modifiers (A, T, HSL)

Sample	a_{av}, %	ΔF_{fr} (N = 5 kN), %	Electrophilic-nucleophilic characteristics of modifier (energy LUMO)
Cu/A/HSL	0.396	–	Electrophile (–1.95) + Nucleophile (10.10)
Cu/T/A	0.491	–18.2	Nucleophile (0.38) + Electrophile (–1.95)
Cu/(A+T)	0.507	–14.3	Nucleophile (0.38) + Electrophile (–1.95)
Cu/A	0.521	–1.4	Electrophile (–1.95)
Cu/HSL	0.532	–	Nucleophile (10.10)
Cu	0.534	–2.2	–
Cu/T	0.568	–1.4	Nucleophile (0.38)

In this study, the nucleophilic-electrophilic properties of active substance molecules of modifiers of metal surfaces were studied using quantum-chemical modelling methods. The properties of molecules were compared with the sorption characteristics of modified metals and antifriction properties in the composition of industrial oil. The donor-acceptor properties of molecules were compared with the adsorption characteristics of the surface of dispersed metals. Considering earlier studies of modification of dispersed metals and the data obtained in this study for antifriction properties in the composition of industrial oil I-20, a relationship between various modes of modification and the hydrophobicity of the surface of dispersed metals was established. The series of enhancement of nucleophilic/electrophilic properties and dipole moment for the used modifiers were obtained. Recommendations for the application of modifiers in practice were offered.

Author contributions

A. G. Syrkov – scientific guidance, editing (40 %). V. R. Kabirov – experimental work, preparation of materials (40 %). A. P. Pomogaybin – technical support for the study (10 %). Ngo Quoc Khanh – work with literary sources, technical support (10 %).

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Syrkov A. G., Bazhin V. Yu., Mustafaev A. S. *Nanotekhnologiya i nanomaterialy. Fizicheskie i mineral'no-syr'evye aspekty* [Nanotechnology and nanomaterials. Physical and mineral aspects]. St. Petersburg: Politekh-Press Publ.; 2019. 244 p. (In Russ.)

2. Syrkov A. G., Pleskunov I. V., Kavun V. S., Taraban V. V., Kushchenko A. N. Changes in the sorption properties of dispersed copper containing ammonium compounds in the surface layer resulting from interaction with water vapours. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2019;21(1): 146–154. https://doi.org/10.17308/kcmf.2019.21/725 (In Russ., abstract in Eng.)

3. Silivanov M. O. *Adsorbtsionnye i kislotno-osnovnye svoistva metallov, soderzhashchikh na poverkhnosti organogidridsiloksan i ammonievye soedineniya i ikh vliyanie na antifriktsionnyi effekt* [Adsorption and acid-base properties of metals containing organohydridesiloxane and ammonium compounds on the surface and their influence on the antifriction effect]. Diss. Cand. Chem. Sciences / Saint Petersburg: Saint-Petersburg State Institute of Technology; 2018. 108 p. Available at: https://search.rsl.ru/ru/record/01008716048 (In Russ.)

4. Syrkov A. G., Silivanov M. O., Sychev M. M., Rozhkova N. N. Alteration of the acid-base properties of the oxidized surface of disperse aluminum during the adsorption of ammonium compounds and the antifriction effect. *Glass Physics and Chemistry*. 2018;44(5): 474–479. https://doi.org/10.1134/s1087659618050206

5. Remzova E. V. *Nelineinost' khimiko-organicheskikh svoistv poverkhnostno-modifitsirovannykh metallov i geterogennykh sistem na ikh osnove* [Nonlinearity of chemical-organic properties of surface-modified metals and heterogeneous systems based on the]. Diss. Cand. Chem. Sciences / Voronezh: Voronezh State University; 2013. 140 p. Available at: https://search.rsl.ru/ru/record/01005058782

6. Slobodov A. A., Syrkov A. G., Yachmenova L. A., Prokopchuk N. R., Kavun V. S. Effect of temperature on solid-state hydride metal synthesis according to thermodynamic modeling. *Journal of Mining Institute*. 2019;239(5): 550–555. https://doi.org/10.31897/pmi.2019.5.550

7. Pleskunov I. V., Prokopchuk N. R., Syrkov A. G., Kabirov V. R. Water-repellent properties of copper powder modified by ammonium compounds during long-term treatment with saturated water vapor. *Proceedings of BSTU Series 2: Chemical technologies. Biotechnology. Geoecology*. 2019;2: 98–105. Available at: https://elibrary.ru/item.asp?id=40802132 (In Russ., abstract in Eng.)

8. Korobochkin V. V., Potgieter J. H., Usoltseva N. V., Dolinina A. S., An V. V. Thermal preparation and characterization of nanodispersed copper-containing powders produced by non-equilibrium electrochemical oxidation of metals. *Solid State Sciences*, 2020;108: 106434. https://doi.org/10.1016/j.solidstatesciences.2020.106434

9. Inamdar A. I., Pathak A., Usman M., Chiou K. R., Tsai P. H., Mendiratta S., Lu K. L. Highly hydrophobic metal–organic framework for self-protecting gate dielectrics. *Journal of Materials Chemistry A*. 2020;8(24): 11958–11965. https://doi.org/10.1039/d0ta00605j

10. Berezhnoi Y. M., Lipkin V. M., Likhota A. D. The influence of polyelectrolytes on the properties of ultramicron and nanosized powders of copper. *Materials Science Forum*. 2018;945: 505–508. https://doi.org/10.4028/www.scientific.net/MSF.945.505

11. Khananashvili L. M., Andrianov K. A. *Tekhnologiya elementoorganicheskikh monomerov i oligomerov* [Technology of organoelement monomers and oligomers]. Moscow: Khimiya Publ.; 1983. 380 p. (In Russ.)

12. Ignat'ev V. M., Emel'yanova N. S., Sanina N. A. Quantum chemical modeling in the system polyvinylpyrrolidone – cation of the dinitrosyl iron complex. *Russian Chemical Bulletin*. 2020;69(12): 2265–2269. https://doi.org/10.1007/s11172-020-3045-7

13. Gribanov E. N., Markov O. I., Khripunov Yu. V. Quantum chemical modeling bismuth-based clusters. *Materials Physics and Mechanics*. 2020;43(1): 72–83. https://doi.org/10.18720/MPM.4312020_9 (In Russ., abstract in Eng.)

14. St. John P. C., Guan Y., Kim Y., Etz B. D., Kim S., Paton R. S. Quantum chemical calculations for over 200,000 organic radical species and 40,000 associated closed-shell molecules. *Scientific Data*. 2020;7(1): 244. https://doi.org/10.1038/s41597-020-00588-x

15. Grambow C. A., Li Y. P., Green W. H. Accurate thermochemistry with small data sets: A bond additivity correction and transfer learning approach. *The Journal of Physical Chemistry A*. 2019;123(27): 5826–5835. https://doi.org/10.1021/acs.jpca.9b04195

16. Kumer A, Sarker M, Paul S. The theoretical investigation of HOMO, LUMO, thermophysical properties and QSAR study of some aromatic carboxylic acids using HyperChem programming. *International Journal of Chemistry and Technology*. 2019;3(1): 26–37. https://doi.org/10.32571/ijct.478179

17. Clark T. *A handbook of computational chemistry: A practical guide to chem. structure a. energy calculations*. New York: Wiley; 1985. 332 p.

18. Nechaev I. V., Vvedenskii A. V. Quantum chemical modeling of the interaction in MeN(H_2O)M (Me = Cu, Ag, Au; N = 1–3; M = 1, 2) system. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2019;21(1): 105–115. https://doi.org/10.17308/kcmf.2019.21/722 (In Russ., abstract in Eng.)

19. Kim A. M. *Organicheskaya khimiya* [Organic chemistry]. Novosibirsk: Izdatel'stvo Novosibirskogo un-ta Publ.; 2002. 844 p. (In Russ.)

20. Lowell S., Shields J. E. Adsorption isotherms. In: *B. S. Powder Surface Area and Porosity*. Dordrecht: Springer; 1984. 320 p. https://doi.org/10.1007/978-94-009-5562-2_3

21. Roberts M. W, McKee C. S. *Chemistry of the metal-gas interface*. Toronto: Clarendon Press; New York: Oxford University Press; 1978. 594 p.

22. Salem R. R. *Fizicheskaya khimiya: Nachala teoreticheskoi elektrokhimii* [Physical Chemistry: Beginnings of Theoretical Electrochemistry]. Moscow: Lenand Publ.; 2021. 320 p. (In Russ.)

23. Pozhidaeva S. V., Ageeva L. S., Ivanov A. M. Comparative analysis of zinc and tin oxidation with acids at room temperatures. *Journal of Mining Institute*. 2018;235(1): 38–46. https://doi.org/10.31897/pmi.2019.1.38

24. Abramzon A. A. *Poverkhnostnoaktivnye veshchestva. Sintez, analiz, svoistva, primenenie* [Surfactants. Synthesis, analysis, properties, application]. Leningrad: Khimiya Publ.; 1988. 200 p. (In Russ.)

25. Hussein O. A., Khudhair D. M., Aljbar A. A. A. A. IR spectroscopic study of triiodosilane ($SiHI_3$) by using semi-empirical quantum program. *Journal of Physics: Conference Series*. 2021;1818 (1): 012014. https://doi.org/10.1088/1742-6596/1818/1/012014

26. Pleskunov I. V., Syrkov A. G., Kabirov V. R. Quantum-chemical modeling of quaternary ammonium compounds for modification of metal surface (Book Chapter). In: *New Materials: preparation, properties and applications in the aspect of nanotechnology*. New York: Nova Science Publishers, Inc; 2020. p. 75–84.

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