

МАШИНОСТРОЕНИЕ И МАШИНОВЕДЕНИЕ MACHINE BUILDING AND MACHINE SCIENCE



UDC 621.893

<https://doi.org/10.23947/1992-5980-2019-19-1-24-30>

Effect of organic acid concentration in lubricant on tribological characteristics of friction couple*

V. E. Burlakova¹, E. G. Droган^{2**}

^{1,2} Don State Technical University, Rostov-on-Don, Russian Federation

Влияние концентрации органической кислоты в составе смазки на трибологические характеристики пары трения***

В. Э. Бурлакова¹, Е. Г. Дроган^{2**}

^{1,2} Донской государственный технический университет, г. Ростов-на-Дону, Российская Федерация

Introduction. The possibility of using monocarboxylic acids as a lubricant composition additive, and the effect of their concentration in lubricant on the evolution of the friction factor of a brass-steel couple, as well as the morphology of the film surface under friction is considered. The work objective is to study the effect of the concentration of carboxylic acids in the lubricant composition on the evolution of the friction factor of copper – steel alloy.

Materials and Methods. Tribological studies of a brass-steel friction couple in aqueous solutions of monocarboxylic acids with the concentrations of 0.025; 0.05; 0.1; 0.2; 0.5 mol/l are carried out. Using scanning electron microscopy, we have studied the morphology of the servovite film surface that is formed on a steel disk after frictional interaction of a brass-steel couple in aqueous solutions of acids with the concentration of 0.1 mol/l.

Research Results. Tribological characteristics of the brass-steel tribocoupling in aqueous solutions of carboxylic acids of various concentrations are studied. The optimum acid concentration in the lubricant composition is specified. Herewith, a selective transfer and a wearless friction regime are implemented under friction of the brass 59–steel 40X couple. A decrease in the friction ratio to 0.009 and 0.007 is found out under friction in aqueous solutions of valeric and caproic acids, respectively. The formation of an anti-friction film on the steel surface is identified through the scanning electron microscopy. It is established that the film formed in an aqueous solution of caproic acid has a denser structure in

Введение. Статья посвящена исследованию возможности использования в качестве присадки к смазочной композиции одноосновных карбоновых кислот и изучению их влияния на эволюцию коэффициента трения пары латунь-сталь, а также изучению морфологии формирующихся при трении поверхности пленок.

Целью работы являлось изучение влияния концентрации карбоновых кислот в составе смазочной композиции на эволюцию коэффициента трения пары сплав медь-сталь.

Материалы и методы. Проведены трибологические исследования пары трения латунь-сталь в водных растворах одноосновных карбоновых кислот с концентрациями 0,025; 0,05; 0,1; 0,2; 0,5 моль/л. С помощью растровой электронной микроскопии изучена морфология поверхности сервовитной пленки, формирующейся на стальном диске после фрикционного взаимодействия пары трения латунь-сталь в водных растворах кислот с концентрацией 0,1 моль/л.

Результаты исследования. Изучены трибологические характеристики трибосопряжения латунь-сталь в водных растворах карбоновых кислот различной концентрации. Установлена оптимальная концентрация кислоты в составе смазки, при которой в результате трения пары латунь 59-сталь 40X реализуется избирательный перенос и достигается режим безызносного трения. Обнаружено снижение коэффициента трения до 0,009 и 0,007 при трении в водных растворах валериановой и капроновой кислот соответственно. С помощью растровой электронной микроскопии выявлено формирование на стальной поверхности антифрикционной пленки. Установлено, что пленка, формирующаяся в водном растворе капроновой кислоты, имеет более плотную структуру, в сравнении с пленкой, формирующейся при трении в водных растворах масляной и капроновой кислот.



* The research is done within the frame of the independent R&D.

** E-mail: vburlakova@donstu.ru, ekaterina.drogan@gmail.com

*** Работа выполнена в рамках инициативной НИР.

comparison with the film formed under friction in aqueous solutions of butyric and caproic acids.

Discussion and Conclusions. Thus, the tribological studies of a brass-steel friction couple in aqueous acid solutions show that the optimum molar acid concentration in the lubricant composition is 0.1 mol/l. At this acid concentration, the values of the friction factor characteristic of the wearless mode are attained.

Keywords: friction factor, wear, selective transfer, servovite film, carboxylic acid, friction surface topography.

For citation: V.E. Burlakova, E.G. Droган. Effect of organic acid concentration in lubricant on tribological characteristics of friction couple. Vestnik of DSTU, 2019, vol. 19, no. 1, pp. 24-30. <https://doi.org/10.23947/1992-5980-2019-19-1-24-30>

Обсуждение и заключения. В результате трибологических исследований пары трения латунь-сталь в водных растворах кислот выявлено, что оптимальной молярной концентрацией кислоты в составе смазки является концентрация 0,1 моль/л. При этой концентрации кислоты достигаются значения коэффициента трения, характерные для режима безызносности. Выявлено, что изменение концентрации кислоты приводит либо к увеличению значений коэффициента трения, либо к незначительному его снижению. При этом увеличение концентрации кислоты сопровождается коррозионными процессами на поверхности пары трения.

Ключевые слова: коэффициент трения, износ, избирательный перенос, сервовитная пленка, карбоновая кислота, топография поверхности трения.

Образец для цитирования. Бурлакова, В. Э. Влияние концентрации органической кислоты в составе смазки на трибологические характеристики пары трения / В. Э. Бурлакова, Е. Г. Дроган // Вестник Донского гос. техн. ун-та. — 2019. — Т.19, №1. — С. 24-30. <https://doi.org/10.23947/1992-5980-2019-19-1-24-30>

Introduction. Modern high-developing machine-building industry advances new demands on lubricants. Most conventional methods of the friction and wear control are based on the use of solid and liquid lubricants [1–4]. The principal function of lubrication in friction units is to keep two contacting surfaces of machine parts from wear. To perform the necessary functions, basic fluids need modification by functional additives that change the antiwear properties of base oils through improving their lubricity among other. For this reason, additives are an integral part of the design of modern lubricants. The studies [2–7] show that to reduce friction and wear, both nanoparticles of metals and various organic components are used as additives to lubricant compositions. Some of them contribute to the formation of protective antifriction films on the tribocontact surfaces due to the presence of metal powders with particle sizes in the micro-range and nanoscale in the lubricant composition [7–9]; others – as a result of selective dissolution of tribo-conjugated surfaces (in the case of copper-steel alloy friction pair) under friction [10–17]. As is known, the lubricating medium plays a critical role in the selective transfer of copper to the steel surface under frictional interaction. For example, during the copper alloy – steel friction, various polar compounds, including carboxylic acids, are formed in the aqueous-glycerin medium. It was interesting to study the possibility of using them as additives to the lubricant composition for implementing a selective transfer and wearless friction.

Materials and Methods. The evolution of the friction factor of the “brass 59-aqueous solution of carboxylic acid – 40X steel” system was investigated on the AE-5 type face friction machine. Aqueous solutions of saturated monobasic carboxylic acids with the general formula: $R-COOH$ ($R = C_nH_{2n+1}$), with the concentrations of 0.025–0.5 mol/l were used as a lubricant composition. Before the tribological studies, samples of steel 40X and brass 59 were cleaned with abrasive paper, washed with distilled water, degreased with hexane, and air-dried. The friction assembly consisted of a steel rigidly fixed disk and three movable brass fingers arranged in a circle at the angle of 120° relative to each other. A friction couple of a ring steel specimen and brass fingers was placed in the lubricant composition into the working part of the friction machine made in the form of a textolite bath. A PHYWE Cobra force sensor was attached to the front face of the working part of the friction machine for continuous recording of the friction variation. Tribological studies were carried out under the following modes: sliding speed of the specimen was 0.45 m/s; axial load was 1.7 MPa; test time was 10 hours; temperature of the working environment was 37° C; slide path was 15,260 m.

The morphology of the servo film was studied using the scanning electron microscopy (SEM) on a Carl ZEISS microscope in the Electron and Optical Microscopy Laboratory and the Center for Collective Use of Scientific Equipment, REC “Materials” (<http://nano.donstu.ru>). The studies were conducted under high vacuum conditions. Accelerating voltage under the scanning mode was 1–3 kV.

Research Results. The dependence of the friction factor on the concentration of carboxylic acid for various volume acid densities under the brass-steel couple friction is given in Fig. 1 and in Table 1. From the analysis of the

data obtained, it follows that the dependence in Fig. 1 is nonmonotonic, with a minimum concentration of acid in the solution of 0.1 mol/l.

Table 1

Dependence of friction factor on acid concentration in lubricant

Lubricant composition, acid solution	Acid chemical formula: R-COOH, where R	Acid concentration, mol/l				
		0.025	0.05	0.1	0.2	0.5
		friction factor, μ				
Formic	-H	0.307	0.348	0.274	0.391	0.545
Acetic	-CH ₃	0.285	0.312	0.258	0.367	0.462
Propionic	-CH ₂ CH ₃	0.195	0.129	0.087	0.239	0.335
Butyric	-CH ₂ CH ₂ CH ₃	0.112	0.083	0.037	0.184	0.307
Valeric	-CH ₂ CH ₂ CH ₂ CH ₃	0.071	0.031	0.009	0.045	0.154
Caproic	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	0.054	0.016	0.007	0.028	0.126

Studying the effect of acid concentration on the friction factor variation in the solution shows that strengthening of formic and acetic acids in the lubricant composition from 0.025 mol/l to 0.05 mol/l leads to the increase in the acidity of the medium and, consequently, to an increase of the values of the friction factor from 0.3 to 0.35.

As a result of frictional interaction, tribocorrosion occurs on the metal surface in the tribosystem. A further increase in the acid concentration to 0.1 mol/l causes a decrease in the friction factor, and then it is accompanied by its sharp increase and strong wear of friction couple materials as a result of the adhesion-mechanical interaction of the protrusions of the surface microrelief (Fig. 1, 2).

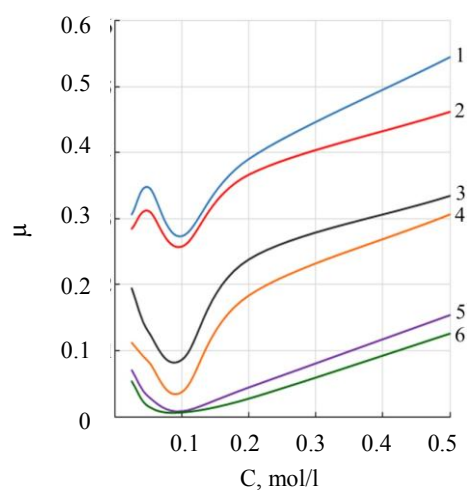


Fig. 1. Dependence of friction factor (μ) on acid concentration (C) in lubricant composition under friction of brass-steel couple: 1 is formic acid, 2 is acetic acid, 3 is propionic acid, 4 is butyric acid, 5 is valeric acid, 6 is caproic acid

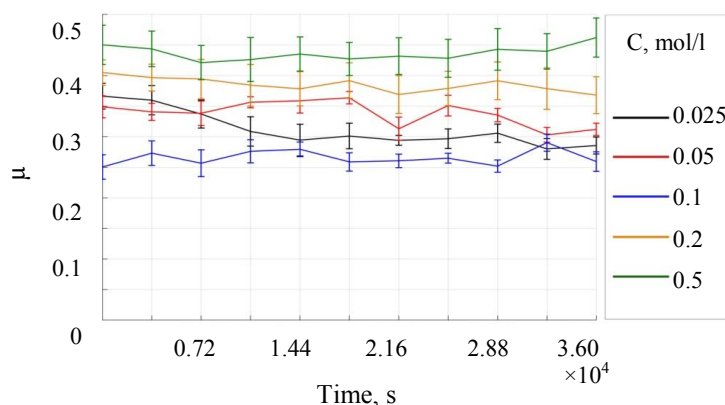


Fig. 2. Evolution of friction factor (μ) on concentration (C) in "brass-aqueous solution of acetic acid-steel" system

A similar dependence of the friction factor on the acid concentration in the lubricant composition is also observed under friction of a brass-steel couple in aqueous solutions of propionic and butyric acids (Fig. 3).

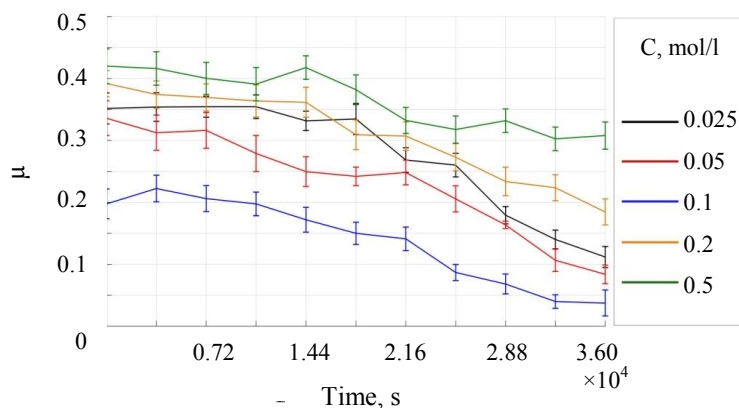


Fig. 3. Evolution of friction factor (μ) on concentration (C) in "brass-aqueous solution of butyric acid-steel" system

At this, the friction factor decreases significantly at the acid concentration of 0.1 mol/l and does not exceed 0.1. A further increase in the acid concentration in the lubricant composition, as well as in the case of formic and acetic acids, is accompanied by its sharp increase (Fig. 1). As a result, wear products are formed in the lubricating fluid volume. In this case, the friction surface is subjected to corrosion-mechanical wear, and the friction factor has rather high values from 0.15 to 0.35 (Fig. 3).

Analysis of the friction factor variation of a brass-steel couple in aqueous solutions of valeric and caproic acids with the concentrations of 0.025 and 0.05 mol/l determines rather low value to 0.07 (Fig. 1, 4).

Application of valeric and caproic acids in a lubricant composition with the concentration of 0.1 mol/l enables to obtain the lowest values of the friction factor to 0.007; optimal conditions for self-organization on the steel surface; the formation of a visually detectable servovite film [13, 18]; and the establishment of a wear-free mode in the tribological system. At this, reduction of the friction factor in the copper-steel alloy couple is associated with the best damping of tribo-film stresses caused by friction.

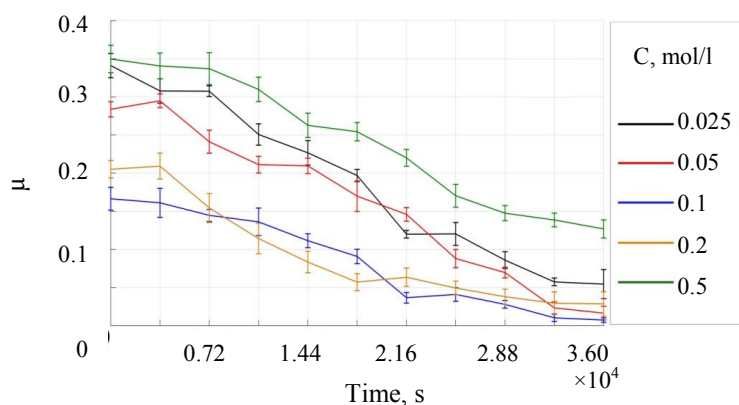


Fig. 4. Evolution of friction factor (μ) on concentration (C) in "brass-aqueous solution of caproic acid-steel" system

Triboelectrochemical reactions occurring in the frictional contact zone in aqueous solutions of valeric and caproic acids not only initiate the formation of a servovite film, which helps to reduce the friction factor, to heal surface microdefects, but intensify the chemisorption which enhances the ordering effect of the substrate on the orientation of molecules under the formation of adsorption acid molecule layer.

Active $-COOH$ polar groups in a carboxylic acid molecule lead to its interaction with metal surfaces with the formation of chemically adsorbed compounds of the bidentate-ligand type [12]. Aliphatic monocarboxylic acids ($R - COOH$) form layers in which the hydrocarbon radicals of the molecules form a closely-packed structure. The adsorbed carboxylic acid molecules on the metal surface not only reduce the friction factor, as compared to a clean friction surface, as it follows from the results obtained, but also increase it. At very low acid concentrations in the solution – to 0.05 mol/l, the degree of filling the adsorption layer is very small; the molecules do not form a continuous film and move freely along the metal surface. Aside from the acid molecules, water molecules can adsorb on the metal surface; however, they do not have an effective shade action, therefore, the friction factor is almost the same as for clean surfaces. As the acid concentration in the solution rises to 0.1 mol/l, the occupancy of the adsorbed friction surface layer

increases, while the acid molecules run parallel to the surface reducing the friction factor as compared to the values for clean friction surfaces. The generated boundary layers at low acid concentrations reduce the friction factor. With further raise of the acid concentration, molecules are arranged perpendicular to the surface; the adsorbed layer increases the surface roughness; and the friction factor grows. The closedness of intermolecular bindings inside the adsorption layer leads to low surface energy and virtual absence of secondary adsorption of acids or other components [19–21].

Analysis of the results obtained through the scanning electron microscopy (SEM) indicates drastic structural changes in the friction surface in acid aqueous solutions when moving from formic to caproic acid (Fig. 4). As can be seen from the SEM visualization of the results obtained, with the relative movement of two surfaces in an aqueous solution of acetic and butyric acids, the surface of the tribocontact has a heterogeneous structure with a large number of pores and irregularities resulting from mechanochemical corrosion; as well as the occurrence of wear particles on the friction surface which causes abrasive wear of rubbing metals. At this, cracks and scratches appear on the friction surface, which significantly reduces wear resistance of the material. Micrographs of the sample surface after friction in aqueous solutions of acetic and butyric acids show major roughness of the friction track, which leads to an increase in the friction factor (Fig. 4a, b). The friction force growth also provokes an increase in temperature in the friction unit, and, as a result, thermal stress of the metal, which is also one of the causes of the crack formation, both on the material surface and in its volume.

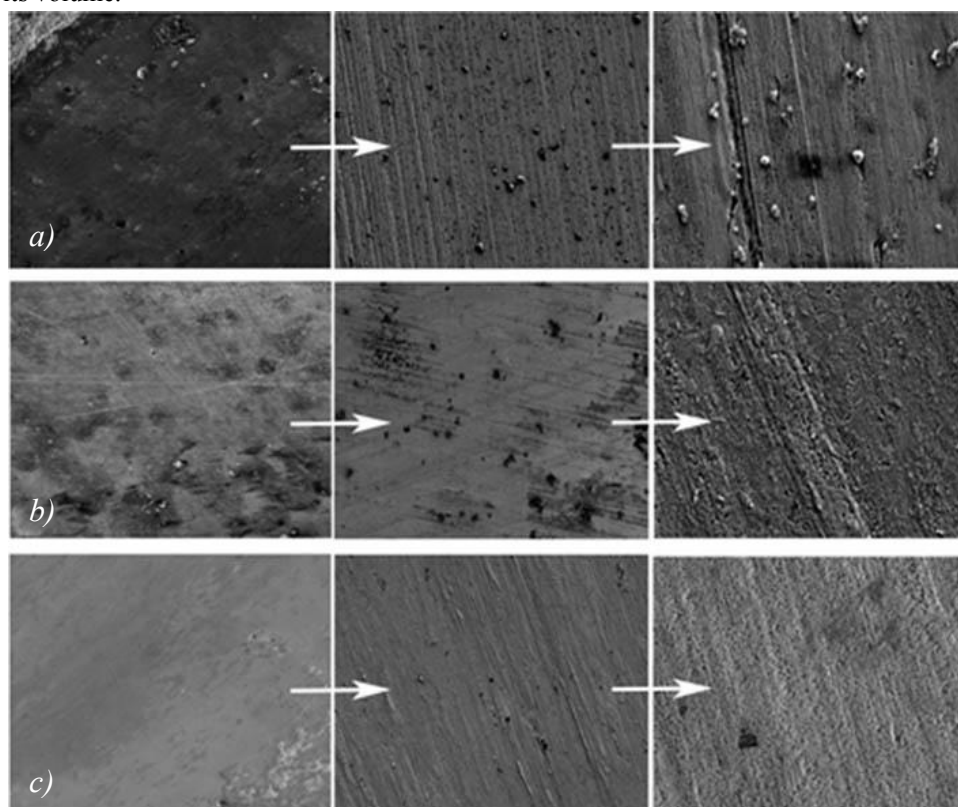


Fig. 5. SEM results of servovite film obtained under friction in “brass-aqueous solution of acid-steel” system:
 (a) is acetic acid, (b) is butyric acid, (c) is caproic acid

When an aqueous solution of caproic acid is used as a lubricant composition under friction of a copper alloy over steel, the formation of a copper non-oxidizing layer on the surface of a steel disk is observed (Fig. 4c) [22]. This effect is explained by the catalytic effect of copper, which converts the lubricant monomers into polymers, ensuring that copper remains in an unoxidized state [12]. Copper film, which is formed through friction in an aqueous solution of caproic acid, has a dense structure with a minimum number of pores, ensuring wearless friction.

Conclusion. As a result of the tribological studies of a brass-steel friction couple in acid aqueous solutions, the optimum acid concentration in the lubricant composition was found. It is established that a change in the acid concentration causes a change in its adsorption on the friction surface, leading to a change in the morphology of the tribo-conjugated surfaces.

References

1. Calhoun, S.F. Antiwear and extreme pressure additives for greases. *Tribology Transactions*, 1960, vol. 3, pp. 208–214. DOI: [10.1080/05698196008972405](https://doi.org/10.1080/05698196008972405)
2. Etefaghi, E., Ahmadi, H., Rashidi, A., Mohtasebi, S. S., Alaei, M. Experimental evaluation of engine oil properties containing copper oxide nanoparticles as a nanoadditive. *International Journal of Industrial Chemistry*, 2013, vol. 4, pp. 1–6. DOI: [10.1186/2228-5547-4-28](https://doi.org/10.1186/2228-5547-4-28)
3. Wu, Y., Tsui, W., Liub, T. Experimental analysis of tribological properties of lubricating oils with nanoparticle additives. *Wear*, 2007, vol. 262, pp. 819–825. DOI: [10.1016/j.wear.2006.08.021](https://doi.org/10.1016/j.wear.2006.08.021)
4. Su, F., Chen, G., Huang, P. Lubricating performances of graphene oxide and onion-like carbon as water-based lubricant additives for smooth and sand-blasted steel discs. *Friction*, 2018, pp. 1–11. DOI: [10.1007/s40544-018-0237-3](https://doi.org/10.1007/s40544-018-0237-3)
5. Kuzharov, A.S., et al. Nanotribologiya vodnykh rastvorov karbonovykh kislot pri trenii bronzy po stali. [Nanotribology of aqueous solutions of carboxylic acids under bronze friction on steel.] *Innovatsii, ekologiya i resursosberegayushchie tekhnologii: materialy XI mezhdunar. nauch.-tekhn. foruma. [Innovation, ecology and resource-saving technologies: Proc. XI Int. Sci.-Tech. Forum.] Rostov-on-Don, 2014, pp. 712–717 (in Russian).*
6. Burlakova, V.E., et al. Vliyanie prirody organicheskoy komponenty na tribotekhnicheskie svoystva sistemy «bronz-aqueous solution of carboxylic acid-steel». [Effect of organic component nature on tribological properties of “bronze-aqueous solution of carboxylic acid-steel” system.] *Vestnik of DSTU*, 2015, vol. 15, no. 4 (83), pp. 63–68. DOI: [10.12737/16067](https://doi.org/10.12737/16067) (in Russian).
7. Yu, H. et al. Tribological properties and lubricating mechanisms of Cu nanoparticles in lubricant. *Transactions of Nonferrous Metals Society of China*, 2008, vol. 18, no. 3, pp. 636–641. DOI: [10.1016/S1003-6326\(08\)60111-9](https://doi.org/10.1016/S1003-6326(08)60111-9)
8. Hu, Z.S., Lai, R., Lou, F., Wang, L., Chen, Z., Chen, G., et al. Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive. *Wear*, 2002, vol. 252, pp. 370–374. DOI: [10.1016/S0043-1648\(01\)00862-6](https://doi.org/10.1016/S0043-1648(01)00862-6)
9. Rastogi, R., Yadav, M., Bhattacharya, A. Application of molybdenum complexes of 1-aryl-2,5-dithiohydrazodicarbonamides as extreme pressure lubricant additives. *Wear*, 2002, vol. 252, no. 9–10, pp. 686–692. DOI: [10.1016/S0043-1648\(01\)00878-X](https://doi.org/10.1016/S0043-1648(01)00878-X)
10. Kragelsky, I.V., Alisin, V.V. *Friction wear lubrication: tribology handbook*. Elsevier; 2016, 263 p.
11. Burlakova, V.E. Triboelektrokhimiya efekta bezyznosnosti. [Triboelectrochemistry of the wearlessness effect.] *DSTU Publ. Centre*, 2005, 211 p. (in Russian).
12. Burlakova, V.E., Milov, A. A., Drogan, E. G. Nanotribology of Aqueous Solutions of Monobasic Carboxylic Acids in a Copper Alloy–Steel Tribological Assembly. *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques*, 2018, vol. 12, no. 6, pp. 1108–1116. DOI: [10.1134/S1027451018050427](https://doi.org/10.1134/S1027451018050427)
13. Burlakova, V.E., et al. Vliyanie sostava smazochnoy sredy na strukturu poverkhnostnykh sloev formiruyushchey pri trenii servovitnoy plenki. [Effect of the lubricating medium composition on the structure of surface layers of a servovite film formed under friction.] *Journal of Surface Investigation. X-Ray, Synchrotron and Neutron Techniques*, 2019, no. 4. DOI: [10.1134/S0207352819040061](https://doi.org/10.1134/S0207352819040061) (in Russian).
14. Myshkin, N.K. Friction transfer film formation in boundary lubrication. *Wear*, 2000, vol. 245, iss. 1-2, pp. 116–124. DOI: [10.1016/S0043-1648\(00\)00472-5](https://doi.org/10.1016/S0043-1648(00)00472-5)
15. Bulgarevich, S.B., Boiko, M.V., Feizova, V.A., Akimova, E.E. Effect of pressure on chemical reactions in the zone of direct friction contact of systems with selective transfer. *Journal of Friction and Wear*, 2011, vol. 32, iss. 3, pp. 145–149. DOI: [10.3103/S1068366611030020](https://doi.org/10.3103/S1068366611030020)
16. Burlakova, V.E., et al. Mekhanicheskie svoystva servovitnykh plenok, formiruyushchikhsya pri trenii v vodnykh rastvorakh karbonovykh kislot. [Mechanical properties of servovite films formed in aqueous solutions of carboxylic acids under friction.] *Vestnik of DSTU*, 2018, vol. 18, no. 3, pp. 280–288. DOI: [10.23947/1992-5980-2018-18-3-280-288](https://doi.org/10.23947/1992-5980-2018-18-3-280-288) (in Russian).
17. Burlakova, V.E., Kosogova, Yu.P., Drogan, E.G. Vliyanie nanorazmernykh klasterov medi na tribotekhnicheskie svoystva pary treniya stal'-stal' v vodnykh rastvorakh spirtov. [Effect of copper nanoclusters on the tribological properties of steel-steel friction pair in alcohol aqueous solutions.] *Vestnik of DSTU*, 2015, vol. 15, no. 2(81), pp. 41–47. DOI: [10.12737/11590](https://doi.org/10.12737/11590) (in Russian).
18. Burlakova, V.E., Drogan, E.G., Gerashchenko, D.Yu. Tribologicheskie vozmozhnosti pary treniya latun'-stal' v vodnykh rastvorakh organicheskikh kislot. [Tribological capabilities of a of brass-steel friction pair in aqueous solutions of organic acids.] *Tribologiya-mashinostroeniye: trudy XII mezhdunar. nauch.-tekhn. konf., posvyashchennoy*

80-letiyu IMASh RAN. [Tribology – to Mechanical Engineering: Proc. XII Int. Sci.-Tech. Conf. dedicated to the 80th anniversary of IMASH RAS.] Izhevsk, 2018, pp. 92–95 (in Russian).

19. Mukhortov, I.V. Polimolekulyarnaya adsorbtsiya smazochnykh materialov i ee uchet v teorii zhidkostnogo treniya. [Multimolecular adsorption lubricants and its integration in the fluid friction theory.] Bulletin of the South Ural State University. Series “Mechanical Engineering Industry”, 2011, no. 31 (258), pp. 62–67 (in Russian).

20. Buyanovskiy, I.A., Ignatieva, Z.V., Levchenko, V.A., Matveenko, V.N. Orientatsionnaya uporyadochennost' granichnykh sloev i smazochnaya sposobnost' masel. [Orientation ordering of boundary layers and lubricity of oils.] Journal of Friction and Wear, 2008, vol. 29, no. 4, pp. 375–381 (in Russian).

21. Novoselova, M.V., Vilms, M.P. Tribologicheskie svoystva tonkikh plenok zhirnykh kislot. [Tribological properties of thin films of fatty acids.] Herald of TvSU. Series “Physics”, 2011, no. 15, pp. 86–91 (in Russian).

22. Garkunov D.N. Scientific Discoveries in Tribotechnologies. No-wear effect under friction: Hydrogen wear of metals, 2007.

Received 12.12.2018

Submitted 20.01.2019

Scheduled in the issue 20.01.2019

Authors:

Burlakova, Victoria E.,

Head of the Chemistry Department, Don State Technical University (1, Gagarin sq., Rostov-on-Don, 344000, RF),
Dr.Sci. (Eng.), professor,

ORCID:<http://orcid.org/0000-0003-3779-7079>

vburlakova@donstu.ru

Drogan, Ekaterina G.,

junior research scholar, Don State Technical University
(1, Gagarin sq., Rostov-on-Don, 344000, RF),

ORCID:<https://orcid.org/0000-0002-4002-2082>

ekaterina.drogan@gmail.com