

# Tribochemical peculiarities of lubricant composition with surface-modified metal powder

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**Abstract.** The influence of different factors (adhesion, surface hydrophobicity, etc.) on antifrictional properties of lubricant with modified metal additives was discussed. The measurements of friction coefficient ( $f$ ) and friction force ( $F_{fr}$ ) were carried out for the heterogeneous systems as oil I-20 with Al-additives modified by triamon (T), alkamon (A) and ethylhydridsiloxane according to various programs. It was established that as a number of T-underlayers, included in Al-additives with chemisorbed external layer of ethylhydridsiloxane reduces from 3 to 1 the force of friction and coefficient of friction reduce. It was discovered that the value of summand which stands for the amount of intermolecular forces in the boundary friction equation can be regulated in Al-additives by using low-molecular T-underlayer.

## 1. Introduction

Consistent (mixed) chemisorption of quaternary ammonium compounds (triamon and alkamon, which are surfactants, based on quaternary ammonium compounds, with molecules having different size) proved to be a potentially successful method of regulation of water repellency, reaction ability and anti-frictional properties of modified metals [1, 2]. The most interesting research objects are modified aluminum samples and Al-containing lubricants. This due to properties listed above and the synergetic effects observed [1–3]. Hydrophobization of metal additives favorably affect anti-frictional properties of lubricants [1, 4], however the influence of location and number of underlayers on metal, with external hydrophobic layer, on adsorption properties of that metal and on characteristics of lubricants is still unknown. Also, fundamental tribological characteristic ( $F_{fr}$  and  $f$ ) of systems with lubricants, which contain disperse metals with multiple layers ( $n = 1–4$ ) of quaternary ammonium compounds and hydrophobic ethylhydridsiloxane, were not yet measured and described. This work's aim was to solve the problems listed above.

## 2. Materials and methods

Aluminum powder (PAP-2) with specific surface area of  $2,6 \pm 0,2$  m<sup>2</sup>/g (BET) was chosen as a primary initial disperse metal. According to transmission electron microscopy (TEM) the size of particles of aluminum powder varies mainly from a few to tens microns, though there are smaller particles, the size of which varies from 45 to 70 nm. Modes of modification, used in the research, do not change a form and a size of particles. Aluminum powder was modified using different modes at a room temperature in vapors of triamon (T), alkamon (A) and hydrophobic silicone-organic liquid (HSL), which is based on ethylhydridsiloxane. Modes of modification of powder were fully described in prior researches [2, 5].

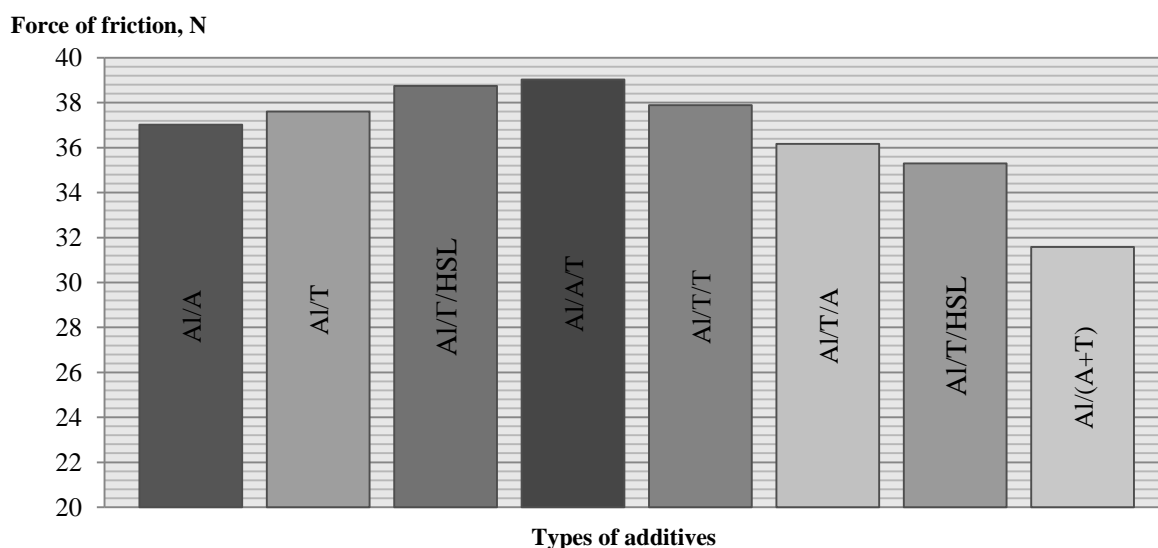


Composition of the samples was determined by using EDX-spectroscopy (analytical attachment EDAX/TSL, shooting mode – 6 kV) and X-ray fluorescence spectroscopy (XRF, Bruker S4 Explorer). The water-repellent properties of the sample were measured gravimetrically using desiccator method at a relative water vapor pressure  $p/p_0 = 0,98 \pm 0,02$ . Al powder, modified in vapors of quaternary ammonium compounds and/or HSL, was added to an industrial oil I-20 (lubricant). Force of friction ( $F_{fr}$ ) and coefficient of friction of the system with oil I-20 with Al-additives was determined by using friction testing machine (DM-29M). The tribological pair was Steel 45 (GOST 1050-88) – Bronze Br Aj 9-4 (GOST 18175-78). Moreover, freshly obtained tribological properties of heterogeneous systems were compared with early obtained integral index of friction ( $D$ ), which is proportional to force of friction. Integral index of friction was measured on certified device ARP-11 (frequency range: 20–300 kHz) using a method of acoustic emission [5].

Samples, based on aluminum powder PAP-2, which were examined, are listed below (except initial Al powder). Al/T – sample with chemisorpted triamon; Al/A – sample with chemisorpted alkamon; Al/(A+T) – sample, treated in vapors of mixture of triamon and alkamon; Al/T/A – sample treated consistently with alkamon and triamon; Al/A/T (changed the consistency of treating) and Al/T/T (2 layers of triamon). In order to examine the influence of number of low molecular triamon underlayers on the properties of external layer of ethylhydridsiloxane (HSL), we synthesized completely new samples (Al/T/HSL, Al/T/T/HSL, Al/T/T/T/HSL). Triamon has a molecular formula of  $[(\text{HOC}_2\text{H}_4)_3\text{N}^+\text{CH}_3][\text{CH}_3\text{SO}_3^-]$ . The main difference between alkamon and triamon is that alkamon has much bigger radicals ( $\text{C}_{16}$ – $\text{C}_{18}$ ) [4].

### 3. Results and discussion

According to figure 1 system with Al/(A+T) sample has the largest decline of coefficient of friction. Al-additive, which modified in vapors of HSL [6] and which has the highest hydrophobicity [5], does not significantly improve the anti-frictional properties of initial lubricant (see also the characteristics of Al/HSL in table 1). The anti-frictional properties significantly improved with inclusion of 1–2 T-underlayers under HSL-layer. Similar effect was discovered for Al/T/A sample, using the friction testing machine DM-29M (figure 1). It is important to note that Al/A/T additive, with alkamon underlayer does not cause  $F_{fr}$  to decrease, as much as Al/T/A does (figure 1, table 1).



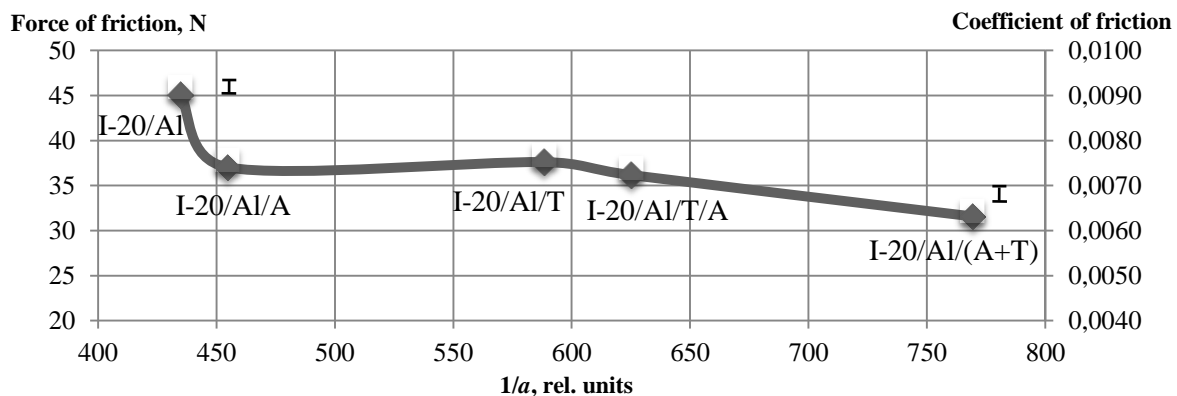
**Figure 1.** Force of friction in systems with lubricants, containing Al-additives, modified using different modes (the weight load was  $N = 5000$  N; lubricants contained 0,5 % of additives by mass).

Modification of aluminum powder in vapors of a mixture (A+T) gives a greater improvement in anti-frictional properties than samples modified in vapors of alkamon or triamon separately (figure 1) [12].

This synergetic effect can be better noticed by the reduction of integral index of friction using acoustic emission method [5]. Setting for acoustic emission (47 MPa) can produce a pressure almost 3 times greater than a friction machine (17 MPa) can. That explains why the value of  $D$  in the decrease of friction in the system with Al/(A+T) is sharper than in the figure 2.

**Table 1.** The influence of type of Al-additive (0,5 % by mass ) on  $F_{fr} = \Phi(N)$  equation, the change of  $F_{fr}$  ( $\Delta F_{fr}$ ) and coefficient of friction ( $f$ ) in comparison with the initial lubricant (I-20).

$N_0$	Al-additive (lubricant)	$F_{fr} = \Phi(N)$ equation	$R^2$	$\Delta F_{fr}$ (average), %	$\Delta F_{fr}$ ( $N = 5 \text{ kN}$ ), %	$f$ ( $N = 3,5 \text{ kN}$ )
1	Al/(A+T)	$y = 0,037x + 12,47$	0,991	-11,41	-15,92	0,0075
2	Al/T/HSL	$y = 0,043x + 12,15$	0,986	-7,42	-5,99	0,0075
3	Al/T/A	$y = 0,048x + 10,81$	0,992	-7,75	-3,69	0,0079
4	Al/A	$y = 0,050x + 12,05$	0,997	-1,05	-1,40	0,0089
5	I-20 (no add.)	$y = 0,050x + 12,29$	0,994	0	0	0,0089
6	Al/T	$y = 0,050x + 11,86$	0,999	-1,52	0,13	0,0087
7	Al/T/T/HSL	$y = 0,049x + 12,49$	0,993	-0,21	0,89	0,0085
8	Al/T/T/T/HSL	$y = 0,048x + 12,50$	0,995	-0,20	0,88	0,0086
9	Al/T/T	$y = 0,051x + 11,59$	0,994	-1,59	0,89	0,0086
10	Al/HSL	$y = 0,048x + 13,22$	0,994	2,32	3,80	0,0086
11	Al/A/T	$y = 0,050x + 12,68$	0,992	1,96	3,95	0,0085
12	Al (PAP-2)	$y = 0,065x + 11,74$	0,997	12,61	20	0,0101



**Figure 2.** The dependence of  $F_{fr}$  and  $f$  on  $1/a$ , where  $a$  – adsorption of water on Al-additive ( $N = 5 \text{ kN}$ ,  $P = 17 \text{ MPa}$ ).

According to the ideas shown in the researches [1, 5, 7], at high load pressure as the liquid lubricant (I-20) is pressed out of the area of contact, system verges in the mode of “dry friction”. Thus, anti-frictional properties of the system significantly depend from characteristics of the surface of solid

additives. Therefore, it becomes evident that in the soft friction conditions the effects caused by physical and chemical properties of Al-additives surface (table 1), become less obvious than in the data shown in and researches [1, 5].

The relationships between frictional force and the weight load of the lubricant with Al-additives and of the original oil I-20 (table 1), can be approximated by the linear with the reliability degree  $R^2$  measured between 0,986–0,999. Obtained  $y = kx + b$  form of equations are similar to the boundary friction equation in which intermolecular interaction of contacting surfaces is considered [8]:

$$F_{fr} = k(N + Sp_0) = kN + kSp_0,$$

where  $k$  – friction coefficient in the measuring range  $N$ ;  $N$  – the force of normal pressure;  $S$  – contact area between solids;  $p_0$  – additional pressure, caused by intermolecular interaction forces.

Equations with minimal proportionality factors  $k$  and the smallest value of  $R^2$  (0,991 and 0,986) correspond to Al-additives (Al/(A+T), Al/T/HSL respectively) which reduce the force of friction the most. Free term of the equation, which is stands for intermolecular interaction, is the smallest for the additive Al/T/A and the biggest for the additive Al/HSL (table 1). Lubricant with Al/T/A ranks among the top three lubricants with the best anti-frictional properties. Otherwise lubricant with Al/HSL has the largest friction coefficient  $f$ .

According to the data shown in the table 1, Al-additives with external HSL-layer on the surface may be placed by the ability to reduce  $F_{fr}$  in the following way:

$$Al / T / HSL > Al / T / T / HSL > Al / T / T / T / HSL > Al / HSL$$



Reduction of  $F_{fr}$

Thus, the additive with one T-underlayer improves the anti-frictional properties of lubricant the most. Such additives as Al/T/T/HSL and Al/T/T/T/HSL have a little positive impact on the  $F_{fr}$  in the weight load range from 50 to 350 kgf. Moreover, they lower the anti-frictional properties of the oil I-20 (in the table 1  $\Delta F_{fr} > 0$ ) at the high weight load (more than 500 kgf).

In the research [9] it was established that the increase in the number of T-underlayers under the external A-layer on the aluminum powder reduces the water-repellent properties of the sample. So, it is possible that the best anti-frictional properties of the sample Al/T/HSL and the increase in hydrophobicity of the sample Al/T/A is just one more example of the monolayer effect, which was derived by Aleskovsky [10]. As a number of T-underlayers increases, the external hydrophobic layer becomes more distanced from the aluminum surface, which leads to the decline of some tribochemical properties of the samples. This fact indicates of influence of force of interaction between the metal surface and the external layer on tribochemical properties of the sample. According to Aleskovsky, after the layering of 3–4 layers the influence of aluminum surface nearly disappears. According to Abramzon [4], hydrophobization of the surface of metal and high level of adhesion between metal and a layer of surfactant are necessary to obtain good anti-frictional and protective properties of the sample. The results of this research confirm that the adhesion factor is a major factor among two factors listed above, which was earlier proved using the acoustic emission method for different metal-fillers [1, 11].

According to the figure 2, the decrease of force of friction in the system is proportional to the decrease of the level of adsorption of the water vapor on the metal. In other words, the force of friction is indirectly proportional to the hydrophobicity of Al-additives.

The similar results were obtained earlier [7]. However, the addition of the water-repellent (A or HSL) on the aluminum does not decrease  $F_{fr}$  of the lubricants by much. The most efficient out of all Al-additives are the additives which have external layer of triamon with the small ( $C_1$ – $C_2$ ) organic substituents on the nitrogen atom. This fact leads to the penetration of the T-molecules to the gaps in the industrially applied stearic nanofilm on the aluminum. We have concluded that the steric availability of the nitrogen atoms in the triamon eases the forming of heteroatomic interaction between nitrogen and metal and between triamon and external layer A or HSL. Factors that are listed above

contribute to the stabilization of the external layer of Al-additive and amplification of the anti-frictional effect of the lubricant with this additive.

Comparing the results to the data obtained for oil I-20 with nanopowder of soft metals (Cu, Zn, Pb, Brass) and received using electroexplosive method [13], shows the following. The synthesized Al-additives allow us to form the lubricants with anti-frictional properties and  $f$ , similar to those in the research [13]. The unusual fact is that due to the presence of micron size particles original disperse Aluminum PAP-2 cannot be named as nanopowder [11]. The  $F_{fr}$  and  $f$  decrease as a result of application of a nanofilm of quaternary ammonium compounds or HSL to a metal surface.

#### 4. Conclusions

Thereby, in the circumstances when concentrations of additives, dispersity of solid-additive, mechanical pressure, the nature of tribological pair, and the temperature of the experiment are equal for all samples; it was found that as a number of T-underlayers included in Al-additives with chemisorbed layer of ethylhydrosiloxane reduces from 3 to 1, the force of friction and coefficient of friction also reduce in heterogeneous systems like oil I-20 with Al-additive. The positive impact of the triamon underlayer on the water-repellent properties of Al-additives and tribosystem with these additives is associated with small molecular size of triamon, steric availability of nitrogen atom, which eases the stabilization of system, as well as adsorptional and anti-frictional properties of the external surface of metal.

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