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Wear Ability of Metal Surfaces in Lubrication with Polycomponent Compositions based on Chemical-Modification Rape-Oil

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The article investigates the processes of bronze-steel pair wear rate during friction on steel 45 (HB 4,45 HPa; Ra_0=0,3±0,05 Mm) during lubrification by chemically modified rapeseed oil with multifunctional additives. The objective of work was to establish the influence of sulphur chemically combined with glycerides of rapeseed oil, and also triphenylphosphine and benzotriazole as multifunctional additives and diphenyl sulphourea as a catalist of sulphidation on wear-resistant properties of compositions. There were used mathematical methods of experimentation planning for obtaining of dependency models of wear rate intensity on ingredients content of lubrification composition and methodology of analysis of the obtained regularities by two-dimensional cross-cuts. As a result, we have received the adequate mathematical models of the second order from four factors with response function – volumetric intensity of wear. By the method of fixing of two factors on certain levels there were received partial mathematical models that enabled two dimensional cross-cuts analysis of dependency of response function on two aspects.

According to the analysis results there was established that the minimal values of wear rate of tin plated phosphor bronze are observed at minimal concentration of sulphur, triphenylphosphine and benzotriazole (0,1-0,2%) and high content of diphenyl sulphourea in the composition. Increase of sulphur content in the composition leads to increase of minimal values of specific wear rate 10-20 times, and increase of triphenylphosphine content at fixed sulphur concentration - 100 times, and narrowing of the respective area.

Key words: wear, steel, bronze, oil, additives, concentration, rapeseed oil, sulfur.

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Introduction

Plant oils have a great potential as independent lubricant materials as disperse environments for composite liquid and viscous lubrications for reduction of metal surfaces' wear rate [1-9]. The research results of properties of plant oils have shown that during heavy-load metal contact the rapeseed oil had the best antifriction and wear-resistant properties for steel lubrication out of 11 plant oils [3, 5]. Besides, base mineral and synthetic oils (excluding polyglycols), majority of their viscosity increasing agents and special purpose additives have low biodegradability level, low coefficient of chemical and biological oxygen uptake, and frequently – toxic [2, 10].

Rapeseed oil significantly excels mineral and synthetic oils in ecological properties [4, 11], but has a chain of essential disadvantages: high chemical activity, and therefore, thermodynamic instability, first of all, at the expence of a big number of unsaturated bonds in the structure of acids' triglycerides; insufficient for disperse environment viscosity; relatively low anti-tearing and wear-resistant properties and protection of metal surfaces from welding at the points of contact during friction and wearing out [12].

Effective method of modification of rapeseed oil glycerides is introduction into their structure of tribo chemically active elements S, P, Cl, that along with forming of high anti-tearing and wear-resistant properties, improve oils' resistance to oxidation [2, 4].

There are methods that may improve these properties of rapeseed oil:

- creation of technological compositions based on polyoxypropylene glycols and rapeseed oil [13];
- triboactivation of chemical processes on metal contact, for example, by introduction of tribopolymeric additive based on cyclic imine[15] in presence of rapeseed oil [14];
- regulation of polarity and functional properties of rapeseed oil and modification of thereof during its treatment by electromagnetic field [16];
- oxyethilation of rapeseed oil or its chemical

modifications [17-19];

- chemichal modifications of rapeseed oil, namely: reduction of nonsaturation via dimerization and polymerization that lead to obtaining of dibasic [4]; reaction of re-esterification [20] by monohydric alcohols (alcohol exchange) and substitution of acyl groups of ester (acidolysis); possible exchange reactions between glycerides [20]; increase of stability of non-saturated molecules of plant oil can be achieved by geometric isomerisation of dibonds and oxidation of its unstable components with further cleaning using activated charcoal and argosites [4]; specific direction is multi-stage chemical processing of rapeseed oil with formation of esters, mono- and dicarboxylic acids, and so on; effective method of modification of rapeseed oil glycerides is introduction into their structure of tribo chemically active elements S, P, Cl, that along with forming of high anti-tearing and wear-resistant properties, improve oils resistance to oxidation [2, 4];
- optimization of multicomponent compositions based on rapeseed oil or its chemical modifications [21-23].

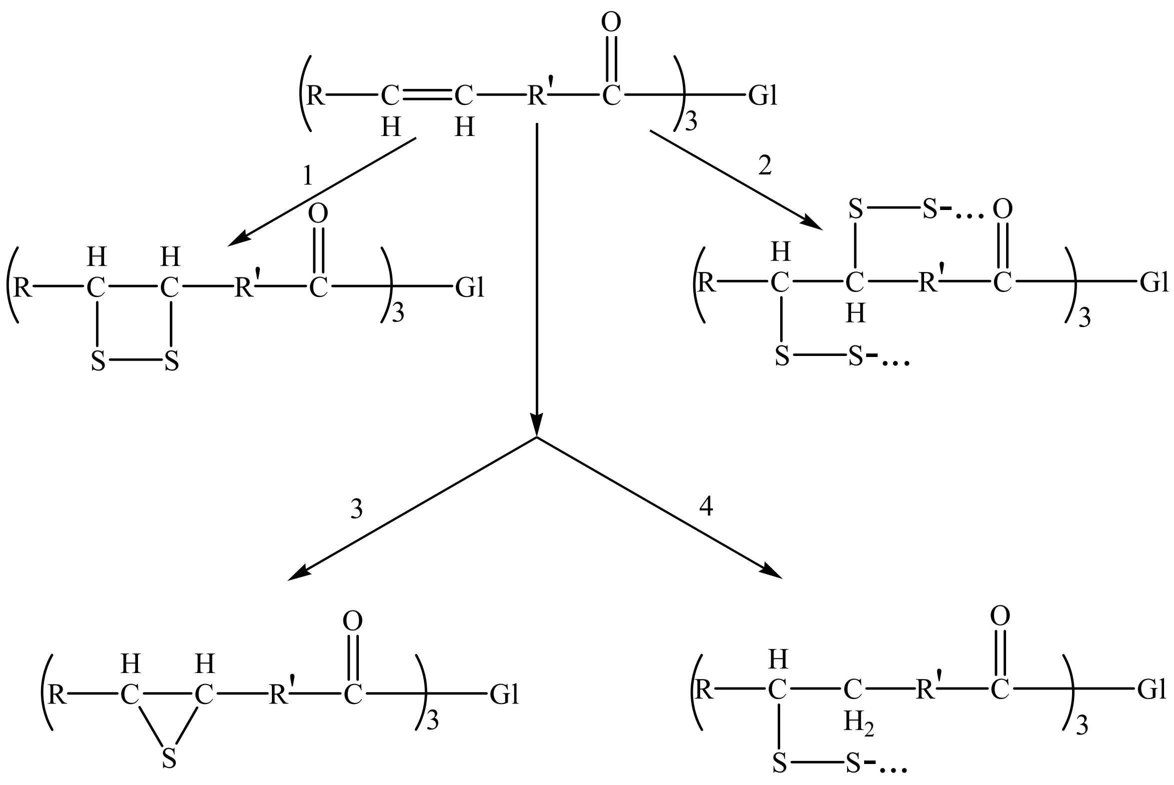
Technology of sulphidation of rapeseed oil is reviewed in [12, 21, 24, 25], properties of the received products – in [26-30], influence of sulphur concentration on products' properties – in [12, 21, 24, 25, 31, 32], and structure of compositions – in [33-36].

The aim of research was to find dependency of steel surface wear rate, and also intensities of tin plated phosphor bronze surface wear rate during friction on steel 45 on reciprocal influence of the components of chemically modified rapeseed oil.

I. Experimental part

1. Technology of sulphidation of rapeseed oil. There was proposed a simple and economically expedient method of chemical modification of rapeseed oil [12], based on the process of its sulphidation at heating till 205-220^{0}C during 1,5-3 hours. Such method enables solution of series of technological tasks: first, to eliminate some essential disadvantages of rapeseed oil (quite high chemical activity and insufficient viscosity); second, to introduce into oil structure active in the zone of fraction sulfide–S –, disulfide –S – S – and polysulfide groups, and thus to supply oil with properties of sulphated additive. Kinetics and duration of this process shall depend on sulphur content added to rapeseed oil. Sulphidation of structure of rapeseed oil will enable use of modified oil as a disperse phase of new oils as additive to basic oils (petroleum and synthetic).

In the process of sulphidation occurs modification of carbon acid residues of rapeseed oil glycerides that can be achieved in different ways: a) conversion of unsaturated residues into saturated through the reactions of addition; b) cross-linking of certain part of acid residues, intra- and intermolecular, increasing molecular weight of rapeseed oil triglycerides, and therefore, its viscosity; c) introduction of sulphur atoms into the structure of acid residues. Thus, the essence of chemical modification of oil triglycerides can be approximately presented by such schemes of intra- and intermolecular reactions:



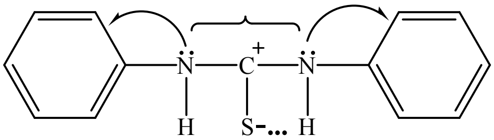
where Gl – glycerine residues of oil triglycerides.

Depending on mass percentage of sulphur introduced during oil sulphidation, it is possible to predict formation of products that vary in viscosity. Thus, introduction of more than 12% of sulphur causes formation of very viscous, and further, quasi-solid products (25%) at the expense of cross-linking of acid residues both by plane and dimensional sulphide and polisulphide groups.

However, it turned out [12] that sulphurized oil also has certain disadvantages, such as insufficient wear-resistant and welding-resistant properties during application in heavy-duty pairs like steel-steel, steel-bronze. With purpose of increasing of antifriction properties of lubrication compositions based on sulphurized rapeseed oil or its mixtures with mineral oils, there was proposed in [33] introduction into their structure of a number of universal additives whose concentration (%) can vary depending on destination of composition: sulphur 1-25%, diphenyl sulphourea 0,1-3,2%, triphenylphosphine 0,1-1,7%, benzotriazole 0,1-1,7%.

Let us consider arguments concerning the choice of reagents:

1. DSU (diphenyl sulphourea) (0,1-3,2%) performs multifunctional role:

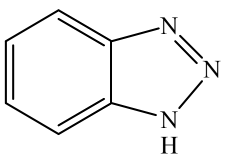


a) catalyst of rapeseed oil sulphidation (without such catalyst the process develops at $210-220^0C$ with significant oxidation destruction); after adding DSU the selectivity of reaction will increase and temperature decrease to $185-190^0C$ (the process developed at $195-200^0C$), and therefore, thermo oxidation destruction of oil glycerides will decrease;

б) at the expense of high polarization of molecules, DSU is anti oxidizer as during the course of sulphidation reaction as during the course of reaction of oil exploitation, and also at the expense of the reaction of detachment of phenol radicals ($C_6H_5^\bullet$) during heating, that break the development of oxidizing chains;

в) DSU – inhibitor of corrosion at the expense of influence of positive center of molecule on the increase of potential value of micro anode areas via absorption of DSU molecules on the surface of metal or alloy in the zone of fraction with such oil.

2. TPP (triphenylphosphine) [$P(C_6H_5)_3$] and BTA (benzotriazole):



are universal anti-wear and anti-tearing additives that are effectively absorbed by fraction surfaces due to high polarity of their molecules (chemosorbtion, Van der Waals' forces) and form near surface chemosorbtion film with oriented structure where specific chemical compounds are formed and decompose (phosphides, sulphides, nitrides of metals, complex combinations of metals and so on), improving tribotechnical characteristics: friction, wear rate, tear index, critical loads, welding. Thus, combination of three quite active elements in the structure of additives (phosphorus, nitrogen, sulphur) at their optimal rate within the oil composition will create maximally possible anti-tear, anti-wear and anti-welding effects during fraction and wear.

2. Technology of preparation of composition:

- **At low concentration of sulphur** (1-8%): DSU is added to rapeseed oil at $60-70^0C$ as catalyst, then finely divided sulphur is introduced and the mixture is heated while stirring (30-35 rpm of mixer) to $195-200^0C$. Appearance of foam at $165-170^0C$ proves the beginning of intensive sulphidation, after which the heating is reduced to temperature growth of $10-15^0C$ per 20 minutes; after 0,5 hour of slow cooling the heating cycle is repeated to $195-200^0C$ and maturing at this temperature of 200 ± 5^0C during 10 minutes. The mass is cooled to 100^0C and nitrogen is flushed through it during 10 minutes, then dissolved at 100^0C alternately during stirring of triphenylphosphine (TPP) and benzotriazole (BTA); mixture is heated at 100^0C during more 10-15 minutes;
- **At high concentration of sulphur** (8-25%): sulphidation is done practically according to the mentioned methodology, but following three stages of heating to $195-200^0C$, moreover DSU is dissolved at the first stage, then 1/3 of sulphur in rapeseed oil, and the rest of sulphur (2/3) is added equally in two stages.

3. Tribotechnical testing. Research of anti-friction properties of oils during lubrication of friction pair steel-steel was done on four balls friction machine: steel balls ШХ-15 (HRC 60-65) diameter 12,7 mm [37, 38]. Index of properties – mean diameter of wear spot per time τ=4 hours at normal load per 3 balls N=300 H (per one ball N_i=123 H), quantity of rotations of upper ball - 1440 per minute (rotation frequency f=24 c^{-1}), number of repeated tests – 3.

Research of functional properties of oils for pair tin plated phosphor bronze 6,5 – 0,15 – steel 45 was performed using three pin tribometer KhTI-72. Three pin friction machine [38] had three cylinder pins of 10±0,1 mm in diameter and 15±0,05 mm in depth with rounded end of r_c =6,35 mm in radius, obtained with help of shaping cutter on lathe, with butt-ends sliding on steel 45 (HB 4,45HPa; Ra_0=0,3±0,05 Mm), speed ν=0,5 m/s, friction sections – 0…10 km – first phase and 10…25 km – second phase. Breaking in was done without lubrication till obtaining of wear scar of the samples of (2±0,1) in diameter provided normal load for one sample of 50N. After breaking in metal surface was cleaned again till Ra_0 =0,2± 0,02 Mm.

Onto the metal surface was applied about 1 mm layer of oil. Conditions during the experiment perfomance: first stage – normal load for one butt-end was 200 N; second stage – normal load for one butt-end 350 N, temperature measured in 1 mm from the surface of the counterbody was 50±2°C.

According to the pressure scheme sphere-plane for steel, constant specific loads varied from the initial pressure p_0=64 MPa<<HB (for tin plated phosphor bronze 6,5-0,15 HB 863 MPa) to pressure p_K.

4. Experiment planning. We used the central composition rotatable plan of the second order for four factors [22-24]: mass percentage of sulphur (S) (X_1), diphenyl sulphourea (X_2), triphenylphosphine (X_3), benzotriazole (X_4). Factors and variance levels are provided in Table 1.

As response functions Y_1 were chosen specific wear rate ($mm^3/N{\cdot}m$) (for pair bronze (tin plated phosphor bronze) 6,5-0,15 – steel 45). Experimental model – polynomial of the second order. Hypothesis of significance of model coefficients was verified using Student's test [41], (insignificant coefficients as compared with experiment deviation were discarded with α=0,05), model adequacy at the level of dispersion of reproduction with α=0,05 was checked using Fisher test [40, 42].

II. Results and discussion

After realization of experiment plan and statistical analysis there was obtained an adequate equation in code values of factors as follows:

$$Y_2 \cdot 10^6 = 0,13 + 0,0448X_1 + 0,0259X_2 + 0,0207X_3 + 0,0296X_4 + 0,0274X_2X_3 + 0,03275X_2X_4 + 0,013 X_2^2 + 0,0105X_4^2. \quad (1)$$

Analysis of the received equations using invariants of determination of the center of the figure and surface appearance [40] has shown that for diameter of wear spot and specific wear intensity of pair tin plated 6,5-0,15 – steel 45 the dependencies of response function of three factors at fixed value of the fourth factor have the form of two-sheet hyperboloid.

When choosing optimal parameters we construct two-dimensional cross-sections of response function (1) for fixed values of two factors that enables to get an idea regarding regularity of change of optimization criterion at varying factors. For this, we have fixed each factor on a certain level (–2; 0; +2), and defined coordinates of a new center S, angular displacement of new axes of coordinates α and transposed the obtained regression equation (2) into canonical as follows:

$$Y - Y_S = B_{jj}X_j^2 + B_{ii}X_i^2. \quad (2)$$

The received results are provided in Table 2.

Figure 1 represents two-dimensional cross-sections of dependency of response functions of specific wear rate for pair tin plated phosphor bronze 4-0,25 – steel 45 on concentration of diphenyl sulphourea (%) and benzotriazole (%) at fixed content values of suphur and triphenylphosphine.

Analysis of these cross-sections at minimal value of sulphur content (C(S)=1%) shows that minimal values of wear rate are observed at minimal concentration of benzotriazole (0,1-0,2%) and high concentration of diphenyl sulphourea in the composition, however the area of low values of response function is very broad and depends on interaction of two factors: concentration of diphenyl sulphourea and benzotriazole, moreover the lines of even values of response

Table 1

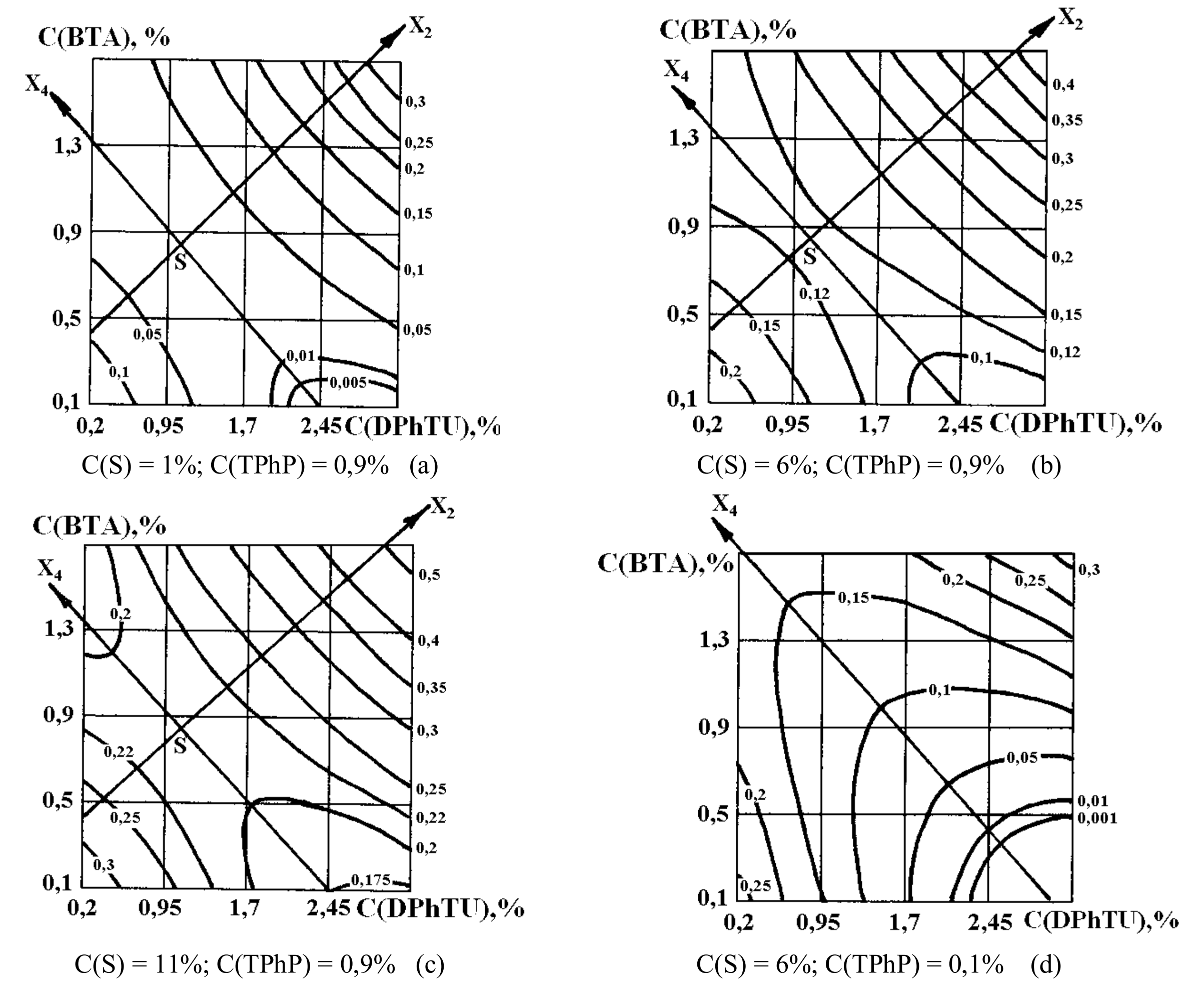
Factors and variance levels

Quantity factors	Components' content, mass percentage			
	S (X_1)	DPhSU (X_2)	TPhP (X_3)	BTA(X_4)
Base level (0)	6	1,7	0,9	0,9
Variance interval	2,5	0,75	0,4	0,4
Upper level (+1)	8,5	2,45	1,3	1,3
Lower level (–1)	3,5	0,95	0,5	0,5
Upper «star point» (+2)	11	3,2	1,7	1,7
Lower «star point» (–2)	1	0,2	0,1	0,1

Table 2

Canonical equations of response function at fixed values of factors

Coordinates of center and angular displacement	Canonical equation
at X_1= –2; i X_3=0: S (–0,8; –0,1); α=42,8^0	$Y–0,0277= 0,0282X_2^2 – 0,0047X_4^2$
at X_1=0; i X_3=0: S (–0,8; –0,1); α=42,8^0	$Y–0,1173= 0,0282X_2^2 – 0,0047X_4^2$
at X_1=+2; i X_3=0: S (–0,8; –0,1); α=42,8^0	$Y–0,2069= 0,0282X_2^2 – 0,0047X_4^2$
at X_1=0; i X_3=–2: S (–3,0; 3,3); α=42,8^0	$Y–0,1801= 0,0282X_2^2 – 0,0047X_4^2$
at X_1=0; i X_3=+2: S (1,4; –3,6); α=42,8^0	$Y–0,1743= 0,0282X_2^2 – 0,0047X_4^2$



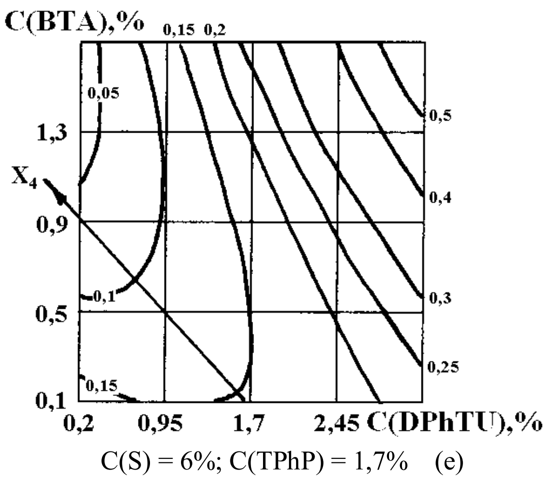


Fig. 1. Two-dimension cross-sections of dependency of response function of specific wear rate (mm^3/N·m) of tin plated phosphor bronze 6,5-0,15 during frinction on steel 45 on concentration of diphenyl sulphourea (%) and benzotriazole (%) at fixed values of sulphur and triphenylphosphine content. The curves of even values of response function provide specific wear rate values for bronze sample [mm^3/N·m].

functions' minimal values correspond to compositions with high concentration of diphenyl sulphourea and low concentration of benzotriazole or vice versa. Concomitant increase of X_2 and X_3 leads to increase of response function. Increase of sulphur content in the composition leads to increase of minimal values of specific wear rate 10-20 times (Fig. 1 b-c), while coordinates of the new center remain unchanged. The nature of dependency does not change as well, but the area of minimal values narrows and corresponds to the compositions with high concentration of diphenyl sulphourea and minimal concentration of benzotriazole.

At minimal value of triphenylphosphine content (Fig. 1d) minimal values of response functions are observed in compositions with high concentration of diphenyl sulphourea and benzotriazole content of 0,1-0,5%. Reduction of diphenyl sulphourea concentration and increase of benzotriazole content leads to increase of target function. At low concentration of diphenyl sulphourea in the composition (0,5-1,3%) wear rate does not depend on benzotriazole content, and at high concentration of benzotriazole in the composition it does not depend on diphenyl sulphourea content.

Increase of triphenylphosphine at fixed sulphur content leads to alteration of coordinates of a new center and increase of wear rate. At triphenylphosphine concentration = 1,7% (Fig. 1e) the minimal values of response function are observed in the compositions with minimal diphenyl sulphourea and high benzotriazole content. At diphenyl sulphourea concentration = 1-2%, and triphenylphosphine concentration = 1,7% wear rate almost does not depend on benzotriazole content.

Maximal values of response function are observed in the compositions with maximal content of diphenyl sulphourea and benzotriazole (in the range of factor space). For low content diphenyl sulphourea and benzotriazole compositions the target function almost does not depend on triphenylphosphine content.

Conclusions

1. Minimal values of wear rate of tin plated phosphor bronze are observed at minimal concentration of sulphur, triphenylphosphine and benzotriazole (0,1-0,2%) and high content of diphenyl sulphourea in the composition. Increase of sulphur content in the composition leads to increase of minimal values of specific wear rate 10-20 times, and increase of triphenylphosphine content at fixed sulphur concentration – 100 times, and narrowing of the respective area.

2. At concentration of sulphur = 1 % and benzotriazole = 0,9 % in the range of factor space, wear rate of the materials is $(0,01 - 0,08)\times10^{-6}$ $mm^3/N{*}m$ and depends on triphenylphosphine and diphenyl sulphourea, moreover the lines of even values of response function correspond to lubrication compositions with high concentration of diphenyl sulphourea and low concentration of triphenylphosphine or vice versa. At concentration of diphenyl sulphourea =1,3-2% wear rate does not depend on triphenylphosphine content.

3. In diphenyl sulphourea low content compositions the influence of benzotriazole content on wear rate of the materials was not found as well as there was not found the influence of triphenylphosphine content on wear rate of the materials in high content benzotriazole lubrication compositions.

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