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Wear-Resistant Properties of Multicomponent Compositions based on Chemically Modified Rapeseed Oil during Lubrication of Bronze – Steel Pair

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The article investigates dependence of bronze-steel pair wear rate on the content of lubricating composition components based on chemically modified rapeseed oil.

Key words: wear ability, diameter of pattern of wear, intensity of wear, steel, aromatic polyamide, oil, concentration, rape-oil, sulfur.

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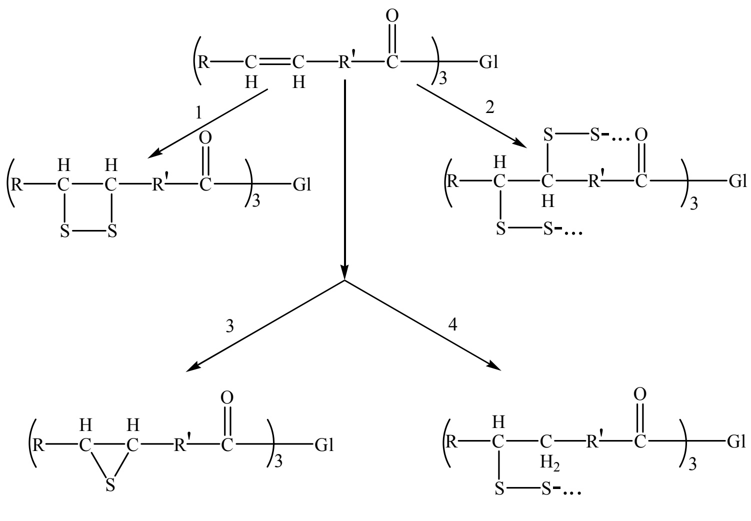
Introduction

Rapeseed oil significantly excels mineral and synthetic oils in ecological properties [1, 2], 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 [3].

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 [1, 4].

Technology of sulphidation of rapeseed oil is reviewed in [3, 5-7], properties of the received products – in [8-12], influence of sulphur concentration on products' properties – in [3, 5-7, 13, 14], and structure of compositions – in [15-18].

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 [3] 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 [15] 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%.

Research objective was to find dependency of tin plated phosphor bronze surface wear rate during friction on steel 45 on mutual influence of the components of chemically modified rapeseed oil.

I. Experimental Part

1. Technology of preparation of composition is explained in [19].

2. Tribotechnical tests. High sensitiveness of point contact to the processes that accompany friction and wear induced us to choose for our experiment the scheme of contact of adjacent surfaces "sphere – plane". Research of functional properties of oils for pair tin plated phosphor bronze 6,5 – 0,15 – steel 45 was performed using three pin tribometer XTI-72. Three pin friction machine [20, 21] 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 4,45 HPa; 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.

3. 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 function $У_1$ was chosen specific wear rate (mm^3/N·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 [42], (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 [23, 25].

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

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:

$$У_2\cdot 10^6=0,13+0,0448X_1+0,0259X_2+0,0207X_3+0,0296X_4+0,0274X_2X_3+0,03275X_2X_4+0,013\,X_2^2+0,0105X_4^2. \quad \mathbf{(1)}$$

Analysis of equations using invariant determination of the figure center and type of surface [23] has shown that for specific wear rate dependency of response function on three factors at the fixed value of the fourth factor was presented by two-sheeted hyperboloids.

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 (1) into canonical as follows:

$$У - У_S = B_{jj}X_j^2 + B_{ii}X_i^2 \quad \textbf{(2)}$$

The received results are provided in Table 2.

Table 2

Canonical equations of response function at fixed values of factors

Coordinates of center and angular displacement	Canonical equation	
at X_1=–2; and X_3=0: S (-0,8; -0,1); α=42,8^0	$У-0{,}0277= 0{,}0282X_2^2 - 0{,}0047X_4^2$	**(3)**
at X_1=0; and X_3=0: S (-0,8; -0,1); α=42,8^0	$У-0{,}1173= 0{,}0282X_2^2 - 0{,}0047X_4^2$	**(4)**
at X_1=+2; and X_3=0: S (-0,8; -0,1); α=42,8^0	$У-0{,}2069= 0{,}0282X_2^2 - 0{,}0047X_4^2$	**(5)**
at X_1=0; and X_3=-2: S (-3,0; 3,3); α=42,8^0	$У-0{,}1801= 0{,}0282X_2^2 - 0{,}0047X_4^2$	**(6)**
at X_1=0; and X_3=+2: S (1,4; -3,6); α=42,8^0	$У-0{,}1743= 0{,}0282X_2^2 - 0{,}0047X_4^2$	**(7)**
at X_1=-2; and X_4=0: S (-0,8; -0,2); α=32,3^0	$У-0{,}0283= 0{,}0217X_2^2 - 0{,}0087X_3^2$	**(8)**
at X_1=0; and X_4=0: S (-0,8; -0,2); α=32,3^0	$У-0{,}1179= 0{,}0217X_2^2 - 0{,}0087X_3^2$	**(9)**
at X_1=+2; and X_4=0: S (-0,8; -0,2); α=32,3^0	$У-0{,}2075= 0{,}0217X_2^2 - 0{,}0087X_3^2$	**(10)**
at X_1=0; and X_4=-2: S (-0,8; 1,8); α=32,3^0	$У-0{,}1422= 0{,}0217X_2^2 - 0{,}0087X_3^2$	**(11)**
at X_1=0; and X_4=+2: S (-0,8; -2,2); α=32,3^0	$У-0{,}1775= 0{,}0217X_2^2 - 0{,}0087X_3^2$	**(12)**

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 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.

Figure 2 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 triphenylphosphine (%) at fixed values of sulphur and benzotriazole content. Analysis of these cross-sections at minimal sulphur content (Fig. 2a) shows that minimal values of response function are observed for broad area of factor space at diphenyl sulphourea concentration (1,5-3,2%) and minimal concentration of triphenylphosphine (0,1-0,3%) or for compositions with high content of triphenylphosphine and low content of diphenyl sulphourea. At sulphur concentration =1% and benzotriazole concentration =0,9% in the range of factor space, wear rate for compositions is (0,01-0,08)×10^{-6} mm^3/N·m and depends on content of triphenylphosphine and diphenyl sulphourea, moreover the lines of even values of response functions correspond to the compositions with high concentration of diphenyl sulphourea and low concentration of triphenylphosphine or vice versa. Concomitant increase of X_2 and X_3 content in the composition leads to increase of target function values approximately 3 times as compared with low content compositions.

At concentration of diphenyl sulphourea =1,3-2% wear rate does not depend on triphenylphosphine content. Increase of sulphur content in the composition leads to increase of minimal values У: 8 times at concentration =6% (Fig. 2b) and 18 times at concentration =11% (Fig. 2c), and narrowing of their area. The coordinates of the new center and nature of dependency remain unchanged. Maximal values of response function increase 1,5 times.

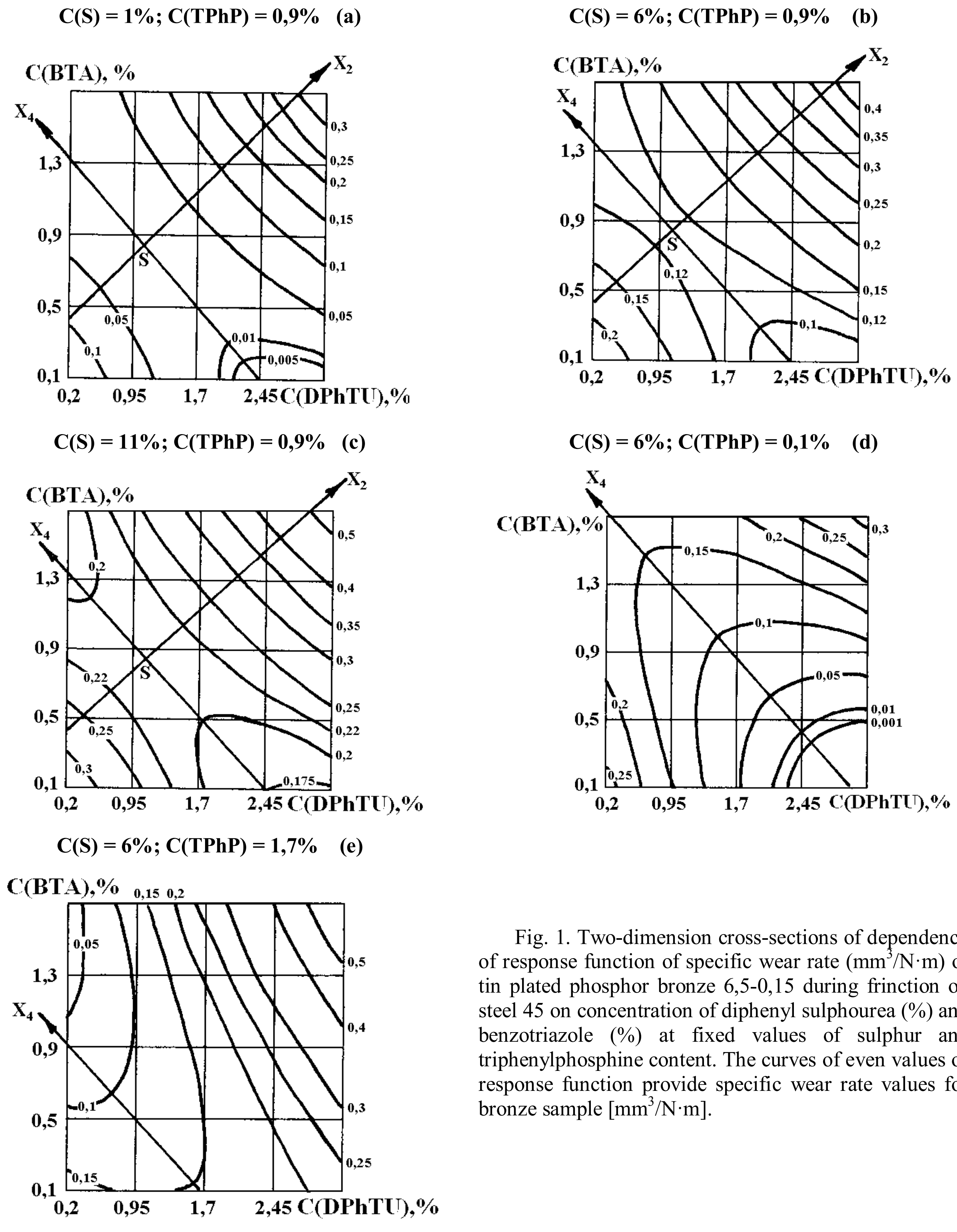
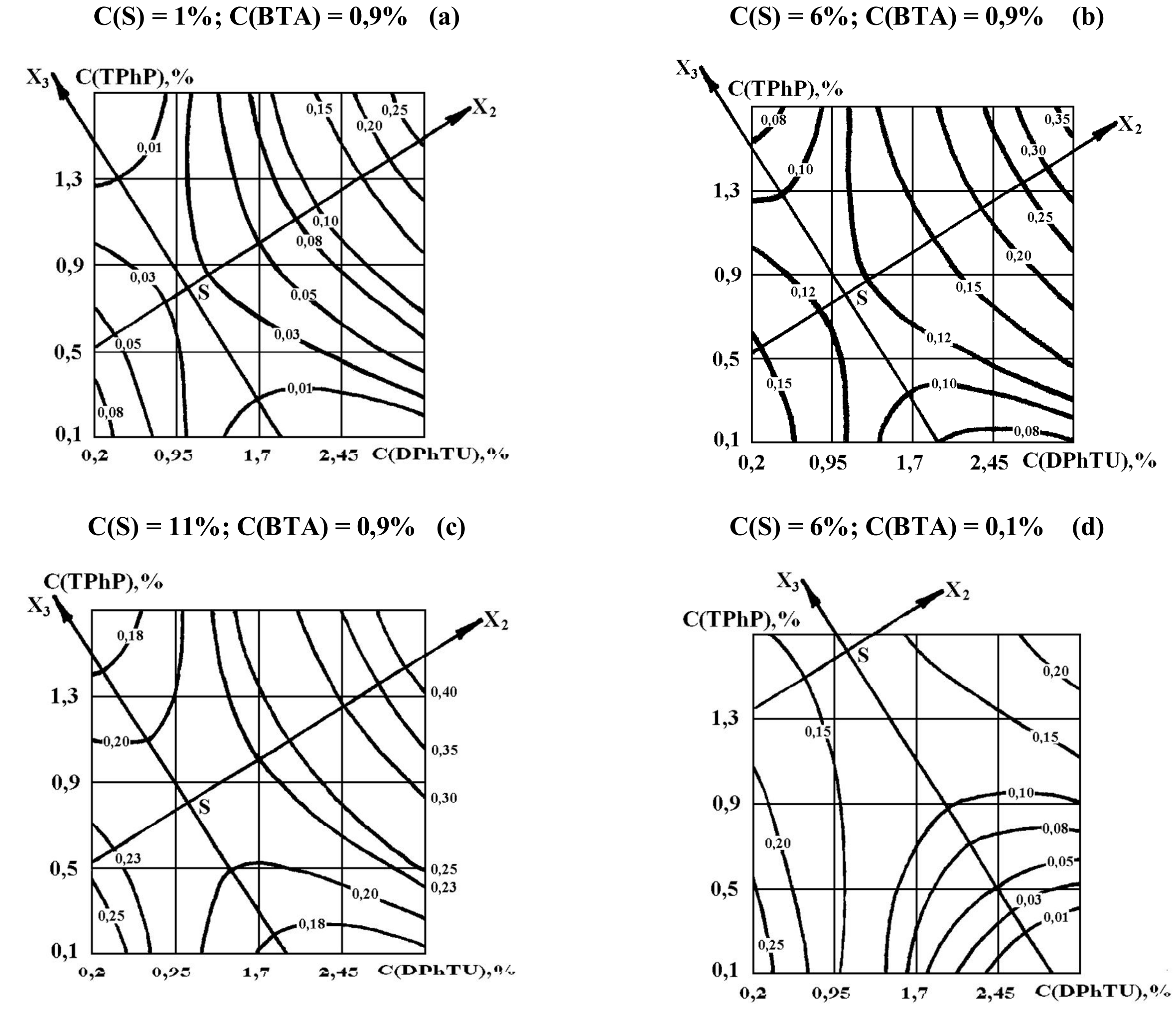


Fig. 1. Two-dimension cross-sections of dependency of response function of specific wear rate (mm^3/N·m) of tin plated phosphor bronze 6,5-0,15 during frinction on steel 45 on concentration of diphenyl sulphourea (%) and benzotriazole (%) at fixed values of sulphur and triphenylphosphine content. The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



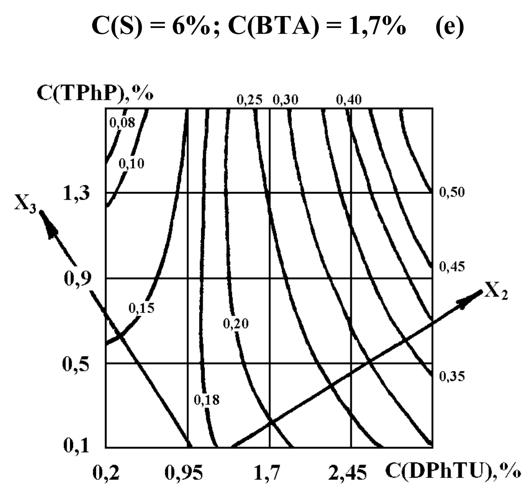


Fig. 2. Two-dimension cross-sections of dependency of response function of specific wear rate (mm^3/N·m) of tin plated phosphor bronze 6,5-0,15 during frinction on steel 45 on concentration of diphenyl sulphourea (%) and triphenylphosphine (%) at fixed values of sulphur and benzotriazole content. The curves of even values of response function provide specific wear rate values for bronze sample [mm^3/N·m].

At minimal content of benzotriazole (Fig. 2d) minimal values of target function are observed in the compositions with high content of diphenyl sulphourea. The content of benzotriazole varies in the range from 0,1 to 0,7%. Wear rate for low content diphenyl sulphourea compositions almost does not depend on benzotriazole content. Maximal values of response function are observed for low and high content compositions in terms of benzotriazole and diphenyl sulphourea concentration. Increase of benzotriazole concentration leads to increase of wear rate (minimal values – 8 times, maximal values – 2,5 times (Fig. 2e)).

The coordinates of the new center shift to the side of lower values of triphenylphosphine content. At concentration of benzotriazole=1,7% the area of minimal values of target function for diphenyl sulphourea high content compositions with low content of benzotriazole (as compared with Fig. 2d) disappears. Here at, wear rate 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)$\times 10^{-6}$ $mm^3/N*m$ 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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