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BIODEGRADABLE LUBRICANT FOR RAILWAY TRANSPORT

Summary. Boron-containing lubricant for rail-curve lubrication is developed**.** Its effectiveness was proved by series of experiments carried out on different types of friction machines. The mechanism of antiscoring effect of boron-containing additives was analyzed in terms of physical adsorption.

БИОРАЗЛАГАЕМЫЙ СМАЗОЧНЫЙ МАТЕРИАЛ ДЛЯ ЖЕЛЕЗНОДОРОЖНОГО ТРАНСПОРТА

Аннотация. Разработан смазочный материал для контакта колесо-рельс, содержащий борную присадку. Его эффективность была подтверждена серией опытов на различных типах машин трения. Механизм противозадирного действия борной присадки был проанализирован с позиции физической адсорбции.

1. INTRODUCTION

At present large amount of rail and rail-curve lubricants are used throughout the world. In accordance with [1] the application of grease reduces surface damage and subsurface deformation of rail curves. These greases basically consist of petroleum hydrocarbons. After operation these lubricants fall on the railroad tracks and pollute the environment. These lubricants do not decompose in natural conditions and damage ecosystems associated with the rail. Thus ensuring of ecological safety of railway transport isn’t possible without creating eco-friendly lubricants for lubricating “rail-wheel” sliding contact.

With the aim to improve the ecological compatibility of works and equipment, new biodegradable eco-friendly lubricants are developed. These lubricants must ensure environmental safety [2-5]. Also they shouldn’t form toxic compounds during their exploitation, their tribological characteristics should not be worse than those of similar oil lubricants. Development of these lubricants faces some problems which can’t be solved by only replacing base oil. The development process has to consider using of new classes of additives and functional admixtures.

Important to know that widely used traditional additives to oil lubricants damage the environment not less than the base oil of lubricants. For example, heavy-metal salts are present in many commercial additives and make these additives not appropriated for using in eco-friendly lubricants. Thus searching of alternative groups of compounds which are acceptable for eco-friendly lubricants is an important problem studied by researchers throughout the world. In present paper boron-containing compounds were considered as a clue of this problem. High tribological performance of boron compounds as functional additives was stated in a number of literature resources [6-9]. At this work widely available boron compounds such as borax and boron acid are used as anti-scoring additives to glycerin which was applied as a biodegradable lubricant [2].

2. EXPERIMENTAL

The anti-scoring performance of boron-containing additives was estimated using a four-ball friction machine in accordance with the ASTM D4172 and IP-239 procedure [10].

Antifriction and anti-wear characteristics of additives were determined using an end friction machine. The friction unit was three steel pin specimens arranged over 45-mm diameter circle with a step of 120°, arranged perpendicular to the ring counterbody, i.e., steel-45 plate with the outer diameter of D_{out} = 40 mm and the inner diameter of D_{in} =16 mm. The area of contact of the counterparts was 3.14 mm^2. The rotation speed of the pin specimens was 240 rpm. The counterbody was placed in the work space of the friction machine, which was filled with the lubricant so that the plate was covered with a 3–5-mm-thick film of the liquid. The experiment was carried out for 3 h under various loads.

The resource of the lubricants was estimated on II-5018 tribometer. The experimental details are presented in section Results and Discussion.

3. RESULTS AND DISCUSSION

Glycerin was selected as a base for the lubricant because it is biodegradable and nontoxic and it can be used in a wide range of operating temperatures. Also glycerin is able to solute inorganic boron compounds. We studied the effect of boric acid H_3BO_3 and borax $Na_2B_4O_7 \cdot 10H_2O$ as anti-scoring additives. Selected compounds do not form radical particles during friction process and in addition these compounds are widely available and cheap.

The relations between the wielding loads and the additive concentrations are shown in Figs. 1 and 2 for boric acid and borax respectively. In both cases, the tests were repeated three times and the results were averaged.

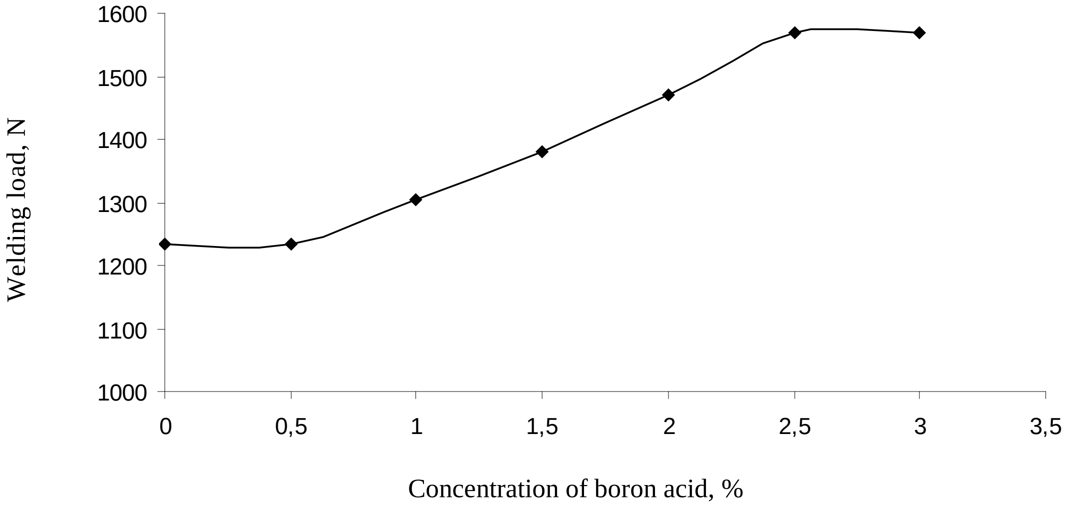

Fig. 1. Relation between welding load and concentration of boron acid
Рис. 1. График зависимости нагрузки сваривания от концентрации борной кислоты

The correlation between wielding load and borax concentration is strong only below 2%. After an increase in borax concentration above 2% the wielding load rising is insufficient. This circumstance suggests the mechanism of the effect of these boron-containing additives as related to friction surfaces interaction. We suppose that this interaction leads to surface films formation and therefore it prevents surfaces from wear and scoring.

Interaction of boron-containing additives with surface was considered as physical adsorption. In accordance with Langmuir equation the adsorption constant can be expressed by (1) [11]:

$$A = A_\infty \frac{KC}{1+KC}, \tag{1}$$

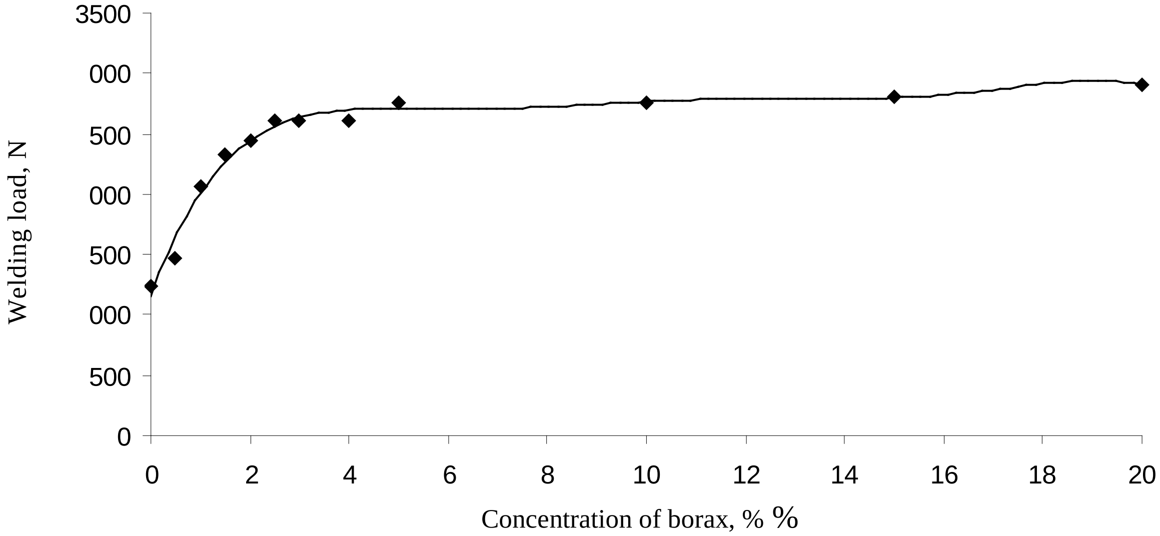

Fig. 2. Relation between welding load and borax concentration
Рис. 2. График зависимости нагрузки сваривания от концентрации буры

where A is the adsorption; A_∞ is the limiting capacity of the adsorption monolayer; C is the mole concentration of the adsorbate in the volume of the solution; and K is the equilibrium constant of adsorption. We considered adsorption capacity of the friction surfaces as a limiting factor of effective additive concentration. An increase in the concentration after friction surfaces are completely covered doesn't have an effect on wielding load. It was assumed that the welding load P_w can be expressed by the following equation:

$$P_w = P_{s,w}(1-x) + P_\infty x, \tag{2}$$

where P_w and P_∞ are the current and maximum welding loads; $P_{s,w}$ is the welding load in the pure solvent; and x is the part of the friction surfaces covered with particles of the adsorbed additive. It was assumed that the ratio A/A_∞ obtained from Eq. (1) is equal to x in Eq. (2); then, from Eqs. (1) and (2), we derived the following equation:

$$\frac{P_w - P_{s,w}}{P_\infty - P_{s,w}} = \frac{KC}{1+KC}. \tag{3}$$

Equation (3) can be transformed to the linear equation (4) for the reciprocal concentration $1/C$:

$$\frac{P_\infty - P_{s,w}}{P_w - P_{s,w}} = \frac{1}{KC} + 1. \tag{4}$$

The percentage concentrations of additives were recalculated to get the mole concentrations on water-free dissolved solution base. The solutions density ρ_{12} was estimated using the following approximate equation: $\rho_{12} = \rho_1\omega_1 + \rho_2\omega_2$ where ρ_1 and ρ_2 are the densities of the solvent and the dissolved substance; and ω_1 and ω_2 are the mass fractions of these substances. For the borax solutions, the dependence of $\frac{P_\infty - P_{s,w}}{P_w - P_{s,w}}$ on 1/*C* was strictly linear in the entire range of the concentrations used; the squared correlation coefficient was r^2 = 0.99. For the boron acid solutions, linearity was only observed at concentrations less than 0.5 mol/L (2.5%); the squared correlation coefficient was r^2 = 0.98. The equilibrium adsorption constant *K* was 227 L/mol for borax solutions and 0.74 L/mol for boron acid solution. These values alone show that borax is more efficient additive than boron acid as it demonstrates better adsorption on the friction surface. From the values of adsorption constants, the increment in the standard isobar potential ΔG^0 of the reaction [12] was found as follows:

$$\Delta G^0 = -RT\ln K \tag{5}$$

where *R* is the universal gas constant and *T* is the absolute temperature. For the adsorption of borax, ΔG^0 = –13.4 kJ/mol and for the adsorption of boron acid, ΔG^0 = 0.7 kJ/mol. These values correspond to physical adsorption [11].

The effectiveness of boron-containing additives was proved by the four ball friction machine tests (Table 1). We studied a change in wear spot diameter for 5% and 20% borax solution for the same test period (10 s).

Table 1

Wear spot diameter as a function of load for various concentrations of solutions of borax in glycerin

Concentration of borax, %		Load, N				
		490	617	784	980	1842
0	Diameter of wear spot d, mm	0,50	1,82	2,01	2,95	3,00
5		0,50	0,59	1,00	1,44	2,06
20		0,30	0,55	0,63	0,72	1,70
Concentration of borax, %		Load, N				
		2067	2450	2607	2764	2800
0	Diameter of wear spot d, mm	3,00	3,00	3,00	3,00	3,00
5		2,64	2,81	2,87	3,00	3,00
20		1,81	1,90	2,05	2,07	3,00

It is clear that the 20% solution is characterized by sufficiently smaller wear spot diameter than the 5% solution. However even 5% additive concentration substantially increases anti-scoring characteristics of lubricant.

The relation between friction coefficient and additive concentration was also studied using the end friction machine (Table 2). The friction coefficient values as well as the wear of steel plate of pure lubricant and borax-containing lubricant are almost equal under low loads but under heavy loads borax-containing lubricant shows better anti-wear performance than pure lubricant.

Data from Table 2 show that 5% borax solution is characterized by slightly higher friction coefficient in comparison with pure glycerin; however, with increasing load, the friction coefficient for 5% borax solution decreases compared with the one for pure glycerin. In addition, this lubricant is characterized by a reduced wear of the plate.

Figure 3 shows the relation between the coefficient of sliding friction and the specific load.

Table 2

Friction coefficient and wear of plate counterbody in glycerin and 5% solution of borax

Specific load applied to pins, MPa	Coefficient of friction for glycerin	Coefficient of friction for 5% solution of borax in glycerin	Wear of plate in glycerin, mm^3/Nm	Wear of plate in 5% solution of borax in glycerin, mm^3/Nm
97	0,29	0,37	$1{,}04\cdot10^{-8}$	$1{,}04\cdot10^{-8}$
194	0,19	0,27	$2{,}50\cdot10^{-8}$	$2{,}92\cdot10^{-8}$
291	0,14	0,21	$4{,}58\cdot10^{-8}$	$5{,}00\cdot10^{-8}$
484	0,10	0,16	$9{,}37\cdot10^{-8}$	$6{,}87\cdot10^{-8}$
970	0,08	0,10	$1{,}56\cdot10^{-7}$	$1{,}19\cdot10^{-7}$
1450	0,09	0,07	$2{,}29\cdot10^{-7}$	$1{,}40\cdot10^{-7}$

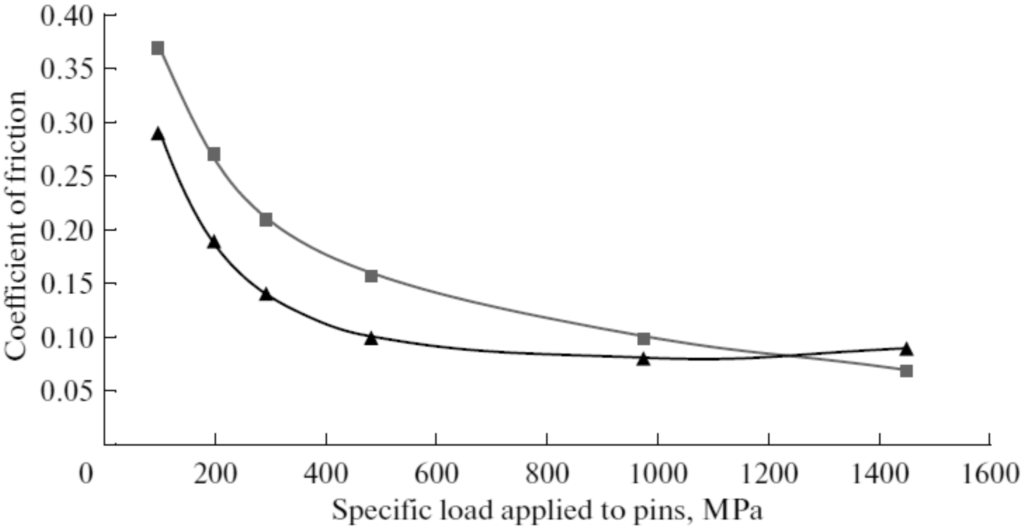

Fig. 3. Relation between the coefficient of friction and applied specific load for (triangles) glycerin and (squares) 5% solution of borax in glycerin

Рис. 3. Зависимость коэффициента трения от приложенной удельной нагрузки для глицерина (треугольный маркер) и для 5% раствора буры в глицерине (квадратный маркер)

The resource of the lubricant was estimated by series of experiments carried out on II-5018 tribometer under the following conditions: the roller made of wheel steel (bottom roller) interacted with the roller made of rail steel (top roller) with a rolling friction with a 10% slip. The lubricant volume of 1 ml was applied on the friction surface of bottom roller. The amount of applied lubricant was equal for all tested friction pairs. The rollers were set in the tribometer and brought into contact. After 300 rotations of the rollers under 980 N load, the rollers were moved out and their non-friction surfaces were cleansed. After that the rollers were weighed and set in the tribometer again. Throughout the test period the friction coefficient was determined. After the friction coefficient values reached 0,1 the experiment was finished. In Table 3 the experimental data obtained for the boron-containing biodegradable lubricant and for the rail-curve lubricant BioRail are presented.

The biodegradability of the lubricants was tested with the method ASTM D5864 Biodegradation Testing for Ready and Ultimate Biodegradation of Fuel, Lubricants and Oil [13, 14]. For all lubricants the biodegradability was not less than 80%.

Table 3

The resource of lubricants

Lubricant	№	The mass of rollers, g		Weight of remaining lubricant film, g	Longevity of lubricants, rot.	Resource of lubricants, rot./g	Average resource of lubricants, rot./g
		before friction	after 300 rotation				
Boron-containing biodegradable lubricant	1	163.142	163.154	0.012	36666	3055500	3174036
	2	163.646	163.658	0.012	34166	2847166	
	3	164.051	164.072	0.021	76008	3619444	
Rail-curve grease BioRail	1	163.305	163.313	0.008	16200	2025000	1983773
	2	163.460	163.467	0.007	14900	1946319	
	3	163.466	163.474	0.008	15840	1980000	

4. CONCLUSIONS

The derived boron-containing lubricant proved to be a promising rail-curve lubricant. The experiments on the four-ball friction machine and the end friction machine demonstrated high anti-wear and anti-scoring characteristics of the lubricant in a friction contact. The comparison of the resources of the developed lubricant with the commercially used biodegradable rail-curve grease also confirmed viability of the derived lubricant in a railway industry. Analyzing the mechanism of anti-scoring effect of boron-containing additives in terms of physical adsorption led to plausible values of the equilibrium constant of adsorption.

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