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## **POLYMERIC COMPOSITE AND LUBRICANTS FOR THE WEARRESISTANT FRICTION UNITS OF RAILWAY MECHANICS**

**Summary.** For long functioning of the friction unit it is necessary to create the steady layers between friction surfaces, which can lower considerably the friction force, and thereof also the wear reducing. Within the metal-polymer tribocoupling the friction transfer film shall function as a separating layer. The frame and kinetics of filming of friction carry at metal- binary material friction is studied, that creates the base for mining new high-performance self-lubricating polymer compositions.

When the unit with a lubricant functions, a role of the uncoupling layer is being fulfilled by the lubricating film, which shall possess the given properties, that is to contain in its composition the nanocluster additives, capable to function in a tribocoupling for a long time, constantly reappearing in a film due to the chemical reactions at friction. It is shown that introduction of nanomodified additives on the basis of phosphorus molybdate of metals into widely used lubricant compositions allows to create steady lubricant films between friction surfaces. The possible mechanism of action of inorganic phosphorous-containing additives of the polymeric nature is discussed.

## **ПОЛИМЕРНЫЕ КОМПОЗИЦИОННЫЕ И СМАЗОЧНЫЕ МАТЕРИАЛЫ ДЛЯ ПОВЫШЕНИЯ ИЗНОСОСТОЙКОСТИ УЗЛОВ ТРЕНИЯ ЖЕЛЕЗНОДОРОЖНОЙ ТЕХНИКИ**

**Аннотация.** Для длительного функционирования узла трения необходимо создать устойчивые слои между поверхностями трения, которые могут значительно понизить силу трения, а вследствие этого и износ. При металлополимерных трибосопряжениях роль разделяющего слоя должна выполнять пленка фрикционного переноса. Исследована структура и кинетика образования пленки фрикционного переноса при трибосопряжении металл-бинарный материал, что создает базу для разработки новых высокоэффективных самосмазывающихся полимерных композиций.

При работе узла со смазкой роль разъединяющего слоя выполняет смазочная пленка, которая должна обладать заданными свойствами, то есть содержать в своем составе нанокластерные добавки, способные функционировать в трибосопряжении длительное время, постоянно возобновляясь в пленке за счет химических реакций

при трении. Показано, что введение наномодифицированных присадок на основе фосфоромолибдатов металлов в широко используемые смазочные композиции позволяет создать устойчивые смазочные пленки между поверхностями трения. Обсужден возможный механизм действия неорганических фосфорсодержащих присадок полимерной природы.

## 1. INTRODUCTION

Special attention of scientists to studying of the friction units of a railway transport rolling stock is caused by specific conditions of their operation, growth of speeds of movement in a combination to high requirements to the brake equipment. For decrease in losses on a friction and wear process it is necessary to establish the reasons of the tribocoupling failure and to develop management methods of tribomechanical, triboelectrical, tribochemical etc processes proceeding on the friction contact [1]. Despite the reached successes, the management problem of friction-contact interaction of mobile metal-polymer elements of the connections remains sharp and unresolved. The effective decision of such problems is possible only on the basis of the fundamental science achievements.

For long functioning of the friction unit it is necessary to create the steady layers between friction surfaces. These layers, separating and interfering with convergence of the friction surfaces, can lower considerably the friction force, and thereof also the wear reducing an intense condition in surfaces areas of rubbing firm bodies.

The effective decision only problems of decrease in intensity of wear process of the wheel pair ridges and the rails head lateral surfaces will allow to increase term of their service ten times almost. The most approved way-creation of lubricant compositions (LC) with certain properties, especially for heavy modes of a friction. So, for a wheel crests and a rail head the deterioration principal view is teases and setting with plastic deformation of metal. Tests on greasing of rails on curve sites have shown, that at using highly effective lubricant the wear process of the carload wheels decreases on 50%, the rails - on 1,5 times.

Thereby, progress on transport is connected with problem of increasing to wear capability of the friction units, in decisions of the last important role plays creation of new polymeric composites and lubricants with given characteristic. This task is very complicated and each of aspect of this problem requires separate investigations. Nowadays it has been reached the understanding that the further development of the science of materials shall be based on regularity of the development of the systems, consisting from a molecular and atomic level objects. Just so they define the main characteristic a substance and processes, running on of the friction contact surface.

## 2. THE COMPOSITE ANTIFRICTION MATERIAL FOR HIGH-GRAVITY LOADED FRICTION UNITS

Within the metal-polymer tribocoupling the friction transfer film shall function as a separating layer, this is being formed in the process of the friction interaction of the metal-polymer pair the polymer forms on the counterbodies, which results in the low friction and high wear resistance. The friction transfer film is the most important microscopic phenomenon, which differs the metal-polymer tribosystems from the metal one. It's known that metal-polymer tribosystems possesses the ability to generate the active destruction products and accumulate the triboelectrical charges. The friction transfer can be carried out as from the whole polymeric composite, as well as from any components mostly. Goal-directed choice of the composite components, concentration composition optimization, and friction transfer mechanism revealing form the base for the new high-effective self-greasing polymeric composition.

The most appropriate methods of the metal-polymer units tribological characteristics improvement are based on using the physical methods of the polymers submolecular structures

modification, what allows to change physical-mechanical and frictional material properties in it a sufficiently wide range without changing their chemical structures [2].

On the basis of the revealed laws of the component frictional division the most effective filling material and the optimum parities of components are established and new highly effective composite self-greased antifriction materials (ASC) are created. Among ASC are allocated with the high characteristics the materials containing in structure the polytetrafluorethylene fibers, possessing low friction factor. The introductions to the composite material the glass fiber having high adhesion to binding are strengthening the composite characteristics. The creation of ASC with two types of fibers allows improving their properties considerably. And adhesive coupling of filling fibers can be varied by modifying of their surfaces.

In particular, developed ASC for sliding support surpasses several times the used domestic materials of similar appointment. Designs variants of various friction units with new materials have been worked and tested: thrust bearing units, plugs of balance weights, the sliding of a lateral support, pantograph bearings etc. Trial check and introduction of the developed materials is carried out at Russian railway enterprises.

The binary metal-polymer materials, where the main load is being taken by the metals (steel, brass, bronze), and high antifriction characteristics are provided by the firm polymeric lubricants, have began using for the heavy-loaded friction units of the railway transport recently. These self-greasing materials are the systems with an anisotropic surface structure, achieving by the constructional way. The main difficulty of these composites creation consists in the necessity of solving of durable fixing solid lubricant (PTFE, PE and others) in the holes and recesses of the supporting structure, receipting the mechanical load. For the low-polar polymers, such as PE and PTFE the filler surface modification is the only possibility of the stable adhesion interface compound creation [3].

By introducing the reactive functional groups into non-polar polymer (by its modification or activation with the help of radiation) the chemical composition of the polymer surface and its properties changing, what results in changing the adhesion interaction character. In particular irradiation of the polymer by x-ray radiation during sufficiently long time brings about origination in it free radicals. It's important that even under small content of the reactive groups the adhesion toughness increases. For instance, introduction even 5-10% active groups into the PTFE surface layer turns out to be sufficient for 10-12-times toughness increase at shift in the system PTFE-epoxy resin [4].

Among the great number of the technological ways of the surfaces polymer modification a special importance have plasmid treatment. For the polymeric materials modification the low-temperature plasma is used basically. Plasma-chemical modification of the surfaces of the solid polymeric material is connected with changing of the chemical composition and structure of the surface layers. In composition of the modified samples the bands, typical for the double and conjugated double bonds ( $1400 - 1750 \text{ cm}^{-1}$ ), as well as for the groups  $\text{CH}_2$  and  $\text{CH}_3$  ( $550 - 700 \text{ cm}^{-1}$ ) have been discovered.

For investigation of the possibility and estimations of the efficiency of the glow discharge using for activation of the PTFE samples surfaces the vacuum installation "Bulat 6,6" was used. The PTFE films were used as samples. The extent of the treatment in the glow discharge of the industrial frequency was estimated by flaking method under the angle  $180^\circ$  of two stuck between each other strips of material. It was found that the activation degree of the fluorine plastic film depends on the pressures of the residual gas in an operating chamber during the treatment. It is the optimum for the given experiment pressure of residual air within  $0,15 \dots 0,25 \cdot 10^{-2} \text{ Pa}$ , under which the maximum degree of activation is reached. The adhesion PTFE activity growth is due to increasing of the cohesion toughness of the surface as a result of the lacing low-molecular fragments of the polymer i.e. on the laced layer base, containing a considerable number of the reactive-able centers, the double bonds  $\text{C}=\text{C}$  firstly, in a thermal treatment process we obtain the polymer with easy polarizing conjugated bonds, stipulating the adhesion of the modified PTFE. The composite surface or it's component modifying gives a possibility of directed friction transfer forming.

Using the complex of the modern physical methods of investigation of the surface phenomena allows to increase and deepen the conceptions of the processes, occurring under modifying polymers

surfaces, as well as find out the main regularities of the formation and kinetics of the friction transfer film obtaining process at the metal-polymer tribocoupling.

### 3. PRINCIPLES OF CREATION OF LUBRICANTS WITH NANOCUSTER ADDITIVES FOR HEAVILY LOADED TRIBOCOUPPLINGS

When the unit with a lubricant functions, a role of the uncoupling layer is being fulfilled by the lubricating film, which shall possess the given properties, that is to contain in its composition the nanocluster additives, capable to function in a tribocoupling for a long time, constantly reappearing in a film due to the chemical reactions at friction. The perspective solution of the specified tasks is an improvement of the lubricants by adding into them the functional additives, varied on the chemical nature and structure. This shall be the economically efficient and ecologically safe types of additives, possessing highly lubricating action.

It's reasonable to lead searching for the new additives of the inorganic nature, which inherent a thermal stability and labored oxidizability and which could not yield on working and tribotechnical characteristics traditionally used ones. Besides if lubricating composition (LC) is used for the heavily-loaded friction units, that it shall contain the inorganic additives with power-intensive chemical bonds, capable to absorb and convert the energy of the contact interaction micro-roughness of the tribocoupling by periodic rearrangement of the molecule's structure. We have started the investigations on development and using of the inorganic polymeric additives, capable to work under high temperatures, which does not make the polymeric matrix of the base less strong and do not allocate at destruction LC harmful gaseous products, promoting construction materials corrosion [5].

The phosphoromolybdates of some metals - lithium, sodium, nickel were chosen as such additives. The anion structure of the compounds  $\text{LiPMoO}_6$ ,  $\text{NaPMoO}_6$  and  $\text{NiP}_2\text{Mo}_2\text{O}_{12}$  consists of phosphate and molybdate radicals, linked by P-O-Mo groups. The variety of the structure, type, shapes and degree of phosphoromolybdates anion polymerization, a wide range of electro-physical and thermal characteristics of the new additives allows to develop goal-directly the methods of obtaining LK with perfected rheological characteristics and form the modified surface layers with high carrier ability. Valuable that synthesized our heteropolyphosphates possesses the ability to exist in an amorphous and crystalline state. Their crystals belong to undermost crystallographic structures – monoclinic and rhombohedric, which turns out to be energetically profitable in conditions of the friction contact.

The experimental data of the electromagnetic heteropolyphosphates characteristics study have shown the prevalence of a covalent bond. It's known that covalent bonds are directed that proves the capacity of moment interactions transmission by them. We expect the moment interactions could be revealed in the torsion interactions, causing the tumbling of the heteropolyphosphatic structure fragments around bond directions that finds the reflection in the infrared spectrum of these compounds. Ability to change the angles between the bonds in the heteropolyphosphatic structure perfects structural adaptability of the additive molecules to the relief of the surface and contributes essential energy to the adhesion interaction. Besides, the polyphosphates are ecological safer than many earlier applicable as additives compounds.

The majority of such polyphosphates dissolves well in various lubricants and don't decompose in the process of their exploitations. These additives can be introduced as into the plastic lubricant of the type Buksol and JRO-M, applicable for the heavily-loaded units of railway machinery, so and in LC for flange and rail greasing of type Puma ML, MG, MP. Introducing the additive of sodium phosphoromolybdate into the plastic lubricant Buksol and JRO-M brings about essential reduction of the friction coefficient and conservation its stable value at time in contrast with these lubricants without such additive [6]. Efficiency of the additive's action is conditioned by its polymeric structure, capacities of the reversible rearrangement of this structure under different condition of tribocoupling operation and its ability to be built into structure of the surface oxide films of rubbing bodies. Essential smoothing of the micro-pattern of friction surfaces have been established by using the sodium phosphoromolybdate in contrast with the lubricants without these additives.

Introduction of these additives into a quantity 1% and 5% into widely using for flange and rail-greasing lubricating compositions of the class Puma has also shown the significant improvement of the tribocoupling [7]. The tribotechnical tests of the initial and nano-modified LC on the four-ball tribometer ЧМТ-1 on the standard method (Tab. 1), as well as on the facing tribometer with flat disks and pair screw rollers under load 1,2 GPA and introduction to zone of the contact different LC. Such design of the tribometer allows controlling the tribocoupling surface condition that is to say presence and stability of the lubricating film in any time lag, not breaking this surface. The operating flat disks were made of steel, close on composition to wheel and rail ones.

The study of stability of the lubricating film on the metal surface in a process of friction have also shown that unlike the pure LC Puma, when in zone of friction after 6 hours of tribocoupling practically does not remain the lubricating film, dealing with LC, including polyphosphate additives in amount of 1%, stable lubricating film is registered on surface of friction after 9 and 12 hours of tribocoupling without accompaniment of lubricant (fig.1).

Table 1

Results or the tribological tests of the greasings Puma-MG and Puma-ML with 1% additives phosphoromolybdates sodium, lithium and nickel

Greasing	Additive	Diameter of the wear stain, mm
Puma-MG	-	0,68
	Phosphoromolybdates sodium	0,42
	Phosphoromolybdates lithium	0,43
	Phosphoromolybdates nickel	0,51
Puma-ML	-	0,64
	Phosphoromolybdates sodium	0,42
	Phosphoromolybdates lithium	0,39
	Phosphoromolybdates nickel	0,52

At investigation of the surface of the tribocoupling on the infrared Furie spectrophotometer Nicolet 380 with HIPO prefix is received that the intensities of the all considered absorption bands on the metal surface well above when using the LC with additives.

Thereby, it is determined, that significant improvement and stabilizations of the lubricants characteristics can be reached by introduction into them the additives on the base of the heteropolyphosphates. The received results can be explained by incessant transformations of the polyphosphates structure at friction that is a distinctive characteristic of inorganic polymers of this sort. It is proved that lubricating film on the surface of metallic counterbody contains the compounds, capable to function in contact during several hours, constantly reappearing in the film by chemical reactions, running at friction. Selecting polymeric phosphate composition, applicable as additives, it is possible, essentially, to dope oxide films of steel and enlarge their protective characteristics relative to influence of high local temperatures in zone of friction contact and to influence of oxidizers of the environment.

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## References

1. Колесников В.И.: *Теплофизические процессы в металлополимерных трибосистемах.* – Наука, Москва, 2003.
2. Колесников В.И., Мясникова Н.А.: *Разработка антифрикционных самосмазывающихся композиционных материалов на основе явления фрикционного переноса.* Вестник РГУПС, №3, 2004. с. 22-25.

3. Колесников В.И., Мясникова Н.А., Кравченко В.Н.: *Фундаментальные основы разработки новых металлополимерных материалов для узлов трения*. Изв. Вузов. Сев.-Кавказ. регион. Техн. науки. Спецвыпуск, 2007, с.12-16.
4. Колесников В.И., Мясникова Н.А., Мясников Ф.В.: *Основы разработки новых самосмазывающихся металлополимерных материалов для узлов трения*. Наука, техника и высшее образование: проблемы и тенденции развития. Материалы 3-ей международной конф. Ростов н/Д: Изд-во РСЭИ, 2008, с. 15-20.
5. Великовский Д.С.: *Присадки к маслам и смазкам на основе продуктов окисления нефтяных углеводородов*. Химия, Москва, 1988.
6. Колесников В.И., Савенкова М.А., Булгаревич С.Б., etc.: *Исследование фрикционных характеристик пластичных железнодорожных смазок с неорганическими полимерами в качестве присадок*. Трение и износ. Т. 29, № 3, 2008, с. 261-267.
7. Колесников В.И., Даниэль Ф., Мясникова Н.А., Савенкова М.А.: *Принципы создания смазочных материалов с нанокластерными добавками для тяжело нагруженных трибосопряжений*. Вестник РГУПС, № 1, 2009, с. 12-15.

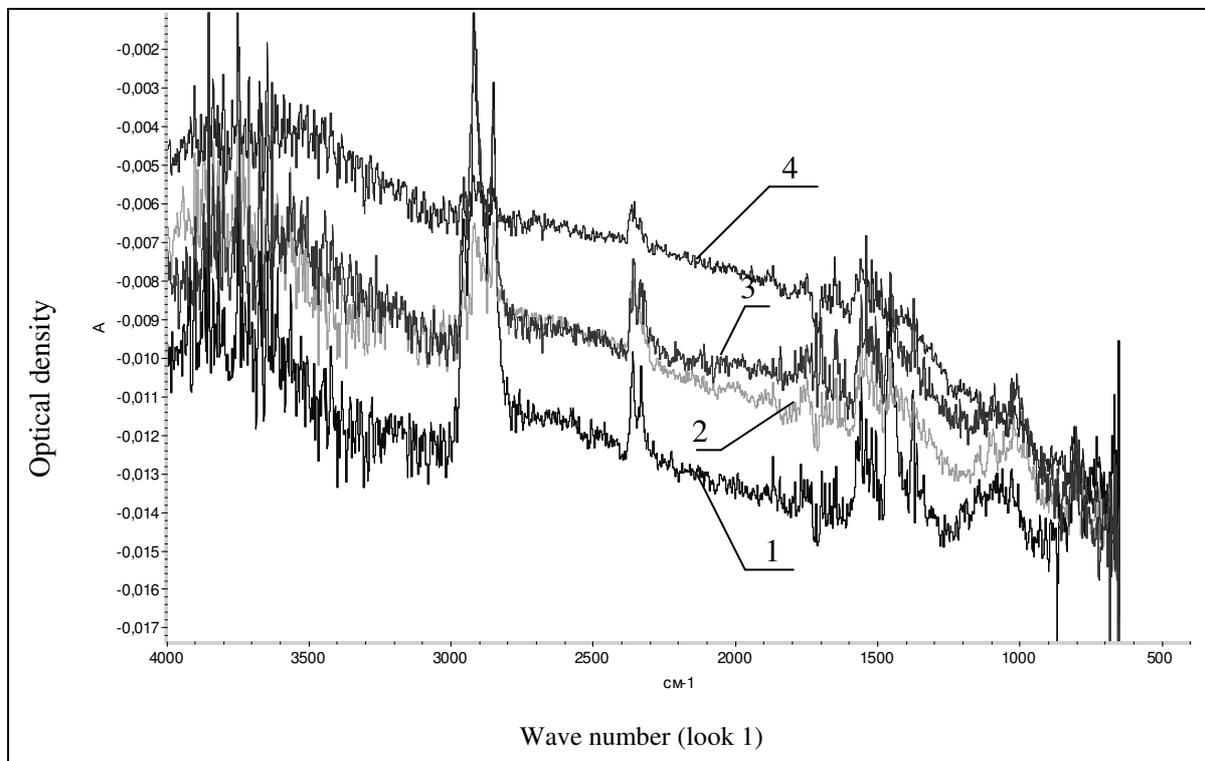


Fig. 1. The IR-spectrum of the metal sample surface after tribocoupling with LC Puma MG+1 %  $\text{NiP}_2\text{Mo}_2\text{O}_{12}$  at various time of contact: 1-1 hour; 2 6 hours; 3 9 hours; 4 - 15 hours

Рис. 1. ИК-спектр поверхности металлического образца после трибосопряжения со СК Пума МГ+1%  $\text{NiP}_2\text{Mo}_2\text{O}_{12}$  при различных временах контакта: 1–1 час; 2– 6 часов; 3– 9 часов; 4 – 15 часов.

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