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Self-organization and Selective Transfer in Tribology

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Abstract: *The focus of the paper is on the phenomenon of self-organization during selective transfer of materials in the contact during the formation of frictional coatings on the surfaces. D.N. Garkunov and G. Polzer were of the first researchers of the selective transfer of material during friction of Cu-containing contact surface with special surface-active substances, where the formed frictional protective coating results in high reduction of friction and wear. The paper also exposes results of the influence of oil-soluble metal-plating composite additive “Valena” in the improvement of tribological properties, e.g. friction, wear and seizure in lubricated contacts, both for oils and greases.*

Key words: *Self-organization, selective transfer, frictional coatings, lubricated contact*

1. Introduction

Spontaneity in the behavior of the tribological system is consequence of an impact given by the examiner for a self-organization, stimulating the release of internal mechanisms for the formation of structures, which are in accord with the self-coordination of the flows of energy dissipation, heat, absorbed energy, wear, temperature gradient, etc. So the system is able to pass from one balance state to another one, more adequate to the external conditions [1-4].

The authors focus on the phenomenon of self-organization during selective transfer of materials in the contact of friction surfaces during the formation of a frictional coating on the surfaces. D.N. Garkunov, I.V.Kragelskii and G. Polzer were of the first researchers [2,3,5-8] of the selective transfer of material during friction of Cu-containing contact surface with special surface-active substances, and the corresponding formation of the frictional protective coating, the so called “servo vitae” layer, results in high reduction of friction and wear. Common works were carried out between the Tribology Center in Sofia and the Tribology Group of Prof. Polzer in Zwickau, and recently in Schoenfels, Germany.

Various publications report that addition of powder copper and its alloys, of tungsten, cadmium, and other metals, molybdenum disulfides, polymers, etc. to lubricants has a favorable effect on friction processes [2,6,8-10]. However, the investigations of the selective transfer mechanism are not as advanced as the traditional tribology of the friction processes. The selective transfer is an appearance of mechanochemistry and physicochemistry of the boundary processes of friction.

These investigations are connected to the battle with the undesired tribological processes of high friction and wear. The specific field of green or environment-friendly tribology emphasizes the aspects of interacting bodies, which are of importance for material and energy sustainability and safety, and which have huge impact upon today’s environment. This includes essentially the control of friction and wear, being of importance for energy, resources, sustainability and cleanness conservation [11-18]. One of the most important tasks of Green Tribology is minimization of wear. Wear limits the lifetime of components and creates the problem of their recycling. Wear can lead to high consumption of the natural resources. Wear creates debris and particles that contaminate the environment and can be even hazardous for humans. Moreover, the large amount of heat generated in the contact joint, also leads to its thermal distortion and failure, and to pollution of the environment with material waste, heat and noise. Measures for minimizing wear are connected to surface processing, namely optimal material selection and surface texturing, coating the surfaces and lubrication. It leads to good health and preservation of performance quality of machines, equipment and production systems, and hence, material, energy and environment saving as a whole [12,19].

Surface coatings are of the most significant measures against wear. A great variety of parameters influences the quality of the coating, depending also on the application. Important characteristics are: thickness, porosity, microstructure, inclusions, cracks, microhardness and adhesion and cohesion bond strength [20]. The search of solution for the task to keep contact surface destruction as small as possible is also aimed in the frictional coating deposition, investigating the process of selective transfer of material between the friction surfaces. In the case of frictional coatings production, this phenomenon is assisted by rubbing of brass against steel under the special conditions of selective transfer [2,6-8, 18,19]. A protective secondary layer is formed in the contact during the process of selective transfer of material between the frictional surfaces. The contact system is composed of brass stick pressed on the coated rotating element with intermediate special lubricant, mostly glycerol, in the contact zone. The interaction in the systems “metal-boundary lubricant-metal” leads to the formation of the frictional surface layer. The self-organization phenomena in this case

depend on the interface energy and the material exchange. Synergy effect in the forming of the new contact structures in the contact between surface materials and lubricant is desirable as optimization of the contact couple. In that case synergy is available, as the two agents - contact surface and lubricant - working together produce a result which is not obtainable by any of the agents independently.

Major results in the use of frictional coatings are the low wear of components coated under condition of selective material transfer mode; the reduction of the concentration of hydrogen at the frictional surface and, respectively, the lower hydrogen wear; the inclination for welding between the friction surfaces is also significantly lowered. A considerable practical result is the possibility for dismantling-free restoration of worn units and couples. Some efficient compositions have been developed.

Further, the outline in the topic embraces also the application of tribological knowledge as enhancement of lubricant quality for better interaction between the working surface and lubricant, and, from the point of view of green tribology, as way of elimination of the lubricant being one of the main sources of environmental pollution [11-15,18].

The paper points up the phenomenon of self-organization during selective transfer of materials in the contact of friction surfaces and the formation of frictional coatings on the surfaces. In this connection, a supplementary item is the presentation of some results from the study of one of the newest additives, the oil-soluble metal-plating composite additive called “**Valena**” manufactured by the company “Rudservice” from Kazakhstan. The development of the additive is based on the scientific discovery and application of the selective transfer of materials between contacting surfaces and no-wear effect, originating with the work of D.N. Garkunov, I.V.Kragelskii, G. Polzer, V. Babel, etc. Influence of this additive on the friction and wear characteristics of bearings and high strength cast iron contact couples lubricated by oils and greases with and without additive has been investigated. Improvement of tribological properties, namely the decrease of friction, wear and seizure is observed in all cases of application of the metal-plating composite additive called “Valena” both in oils and greases [2,6,8,9,21].

According to the authors, investigation of self-organization and selective material transfer offers great potential for application in tribology and tribotechnology, but this would need the cooperation of a wide group of tribologists to gain further knowledge of its internal mechanism and the interaction processes occurring in the surface layers of friction bodies.

2. Self-organization in tribology

The world view of the classical science is based on the Newtonian paradigm of mechanics, where every phenomenon we observe can be reduced to a collection of atoms or particles, whose movement is governed by the deterministic laws of nature. Things that exist now have already existed in the past, and will exist so in the future. In such a philosophy, there seems to be no place for novelty or creativity.

Modern science has come to the conclusion that such a philosophy will never allow us to explain or model the complex world that surrounds us. Around the middle of the last century, researchers from different disciplines started to study phenomena that seemed to be governed by inherent creativity, resulting in spontaneous appearance of novel structures or adaptation to a changing environment. The concepts, methods and principles they developed, have slowly started to combine into a new approach, a science of self-organization and adaptation [1-4,22,23].

Spontaneous emergence of new structures is easy to observe, not only in the laboratory and in our day-to-day world. The most common example is crystallization, the appearance of a symmetric pattern of dense matter in a solution of randomly moving molecules. *Self-organization* is manifested in the appearance of structure without an external agent imposing it.

In its essence, self-organization is the spontaneous creation of a coherent pattern out of the local contact interactions between initially independent elements. This collective order is organized in function of its own maintenance, and thus tends to resist perturbations. A general characteristic of self-organizing systems is that they are *robust* or *resilient*. This robustness is achieved by distributed, redundant, duplicating control so that damage can be restored by the remaining, undamaged sections.

The basic mechanism underlying self-organization is the deterministic or stochastic variation that governs any dynamic system, exploring different regions in the state space until it reaches an attractor, i.e. a configuration that closes in on it. This process can be accelerated and deepened by increasing variation (external perturbation), for example by adding “noise” to the system [23].

Investigation of self-organization and selective material transfer offers great potential for application in tribology and tribotechnology, but this would development and gain of further knowledge about its internal mechanism and about the interaction processes occurring in the surface layers of friction bodies.

In *tribology* there are many effects connected to self-organization: the effect of extremely low friction after irradiation of the surfaces with alpha-particles or ultrasound; the effect of selective transfer of material between the contacting surfaces; the effect of surface-active additives in lubricants which cause decrease of surface strength; the effect of autovibrations, etc. [4]. In all cases formation of new structures is observed – these are secondary protective surface structures. The study of the secondary protective surface structures is a central question in the study of self-organization. Problems of optimizing the tribosystem are related to the possibility of optimizing the conditions, under which a system being introduced in operating regime, forms secondary protective structures. Generally, the affect is on the working surface (material, preliminary structure) and on the conditions of the process, in such way that the *internal* for the system factors of its self-organization could be switched on.

3. Self-organization and selective transfer of material between contacting surfaces. Frictional coatings.

The authors of the present paper spotlight on the phenomenon of self-organization in the duration of selective transfer of materials in the contact of friction surfaces during the formation of a frictional coating on the surfaces, initially studied by D.N. Garkunov, G. Polzer, V. Babel, R. Marczak, etc. [7]. Some results of the basic studies and application in the area of copper frictional coatings are presented below.

3.1. Mechanisms of the selective transfer. Background.

According to **D.N. Garkunov** [2] the frictional film forms on the friction surfaces in the bronze-steel tribocouple with glycerin lubrication passing firstly through dissolution of the bronze surface, where the glycerin acts as a weak acid. The atoms of the elements (tin, zinc, iron, aluminum) absorbed in bronze outgo into the lubricant, and as result the bronze surface is enriched with copper. Friction deformation of the bronze surface causes new passing of elements into the lubricant, so the bronze layer is purified and it nearly contains only copper. Its pores fill with glycerin (the surface porosity is a typical characteristic of the selective transfer [24]). Glycerin is reducer for copper oxides, hence the copper film is free from oxides; it is very active with free ions and is highly adhesive for the steel surface. The steel surface is covered by thin copper layer. Self-organization and selective transfer of copper to steel take place. Before the stabilized selective transfer, the process continues until steel and bronze are coated by 2 μm copper layers [2,5-9,24]. Mechanical and chemical transformations take place; e.g. formation of surface active substances on the friction surfaces; they interact chemically with the surfaces and form chemisorbed layers (see Figure 1).

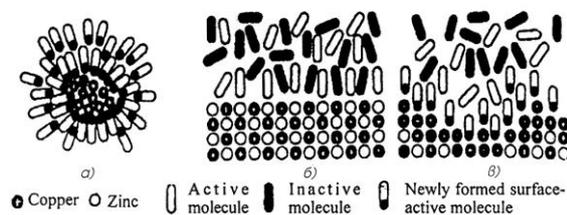


Figure 1 Formation of micelles and interaction of surface-active substances with bronze (as per [24])

One more possible mechanism of the “servo vitae” layer formation during selective transfer was discussed by **N.S. Enikolopyan** [25,26]. High pressures together with shift deformation, which are the necessary main components of the friction process, impart immense chemical and physical energy to the material, and in particular, promote solid monomers’ polymerization at abnormally high reaction velocities. According to the author, this offers great potential for utilization in tribology and tribotechnology.

Gottlieb Polzer studied and implemented in practice direct coating deposition by friction. Based on equation of the theoretical physics, he had formerly derived equations of self-organization at friction [2, 6-8]. Always when destruction problems are available in nature, there is either a simultaneous growth process which involves equilibrium between destruction and regeneration or destruction leads to exponential destroying of the whole system, in our case the tribological couple. The phenomenon frictional coating deposition is assisted by the rubbing/deposition of brass under the special conditions of selective transfer of material. In the contact zones emerges reactive coating deposition with special properties: Copper is rubbed on the steel friction surfaces with totally different electro-chemical potential, and secondly, not only the content but also the structure in the friction surfaces is being changed [6-8].

The element to be coated is both subjected to rotation and to the pressure of a brass stick in the presence of a special lubricant, mostly glycerol. Characteristic for the process of selective transfer of material between the frictional surfaces is the formation of secondary layer with low shift resistance in the contact. This protective layer cannot accumulate dislocations and is highly antifrictional. High pressures together with shift deformation, which are the necessary main components of the friction process, impart immense chemical and physical energy to the material, promoting high reaction velocities. Generation of that layer requires special combination of materials of the contact surfaces, as well as special lubricant between them. As a result, a tribological system appears which can bear higher loads at the influence of various processes. Different machines were designed and constructed at the Department Tribotechnik in Zwickau’ Higher Technical School, corresponding to the principles of the frictional deposition and the ideas of the selective transfer. Many pieces of the devices „MBZ 1” for shaft coatings and „MBZ 3 A” for application in rotating machines were manufactured, e.g. the „MBZ 3 A” (see Figure 2) for engine cylinders was produced in 30 items. Unfortunately there is not sufficient use of the advantages of the deposition of copper frictional coatings in the overall practice.

As said by **George Spenkov**, a qualitatively new stage in the tribological investigation of friction has begun with the study of the selective transfer [27]. The characteristic feature of this stage is closer study of physicochemical processes of contact. This has resulted in the detection of a series of new friction phenomena requiring revision of the traditional methods of wear prevention. Making use of favorable friction phenomena (selective transfer, tribopolymerization, abnormally low friction in a vacuum, etc.) plus wide introduction of new methods for combating the harmful phenomena (e.g. hydrogen wear of metals, seizing etc.) could offer considerable potential economic benefits. This enabled the production of new lubricating materials, using in practice selective transfer during sliding and also theoretical study of this phenomenon. So, the term “selective transfer” became an adopted abbreviation for decreased wear and coefficient of friction, which is a result of non-oxidized thin copper film formation induced by sliding.

Juozas Padgurskas et al. [28] in Lithuania investigate tribology of electro-pulsed copper and brass coats. Friction coefficient and microscopic investigations demonstrated that porous quasi-liquid protective metal film was self-forming when the electro-impulsive sprayed copper and brass coats are operating in friction pair at the marginal lubrication conditions. This film appears because of the selective transfer phenomenon in such friction pairs and determines low friction coefficient, which is characteristic to the liquid lubrication.

3.2. *Effect of the metal-plating additives. VALENA additive.*

Lubricating oil service time depends on its antioxidant property, i.e. its resistance to changes of physico-chemical and service properties during operation and storage. Lubricating oil antioxidant stability is one of the most important properties determining its service period. The less stability is the more often the oil should be changed during operation.

The term *metal-plating lubricant* appeared in 1962 in connection of the invention by D.N. Garkunov in Russia, about a lubricant capable of realization of selective transfer of material between the contacting surfaces [2]. The development continued with the work of Prof. G. Polzer, Prof. V. Babel, Prof. R. Marczak, etc. researchers in the field of selective transfer [2,7-9,18,24]. This class of lubricants contains 0.1 to 3 % of additives: metal powders, alloys and oxides, salts and metal-organic complexes, so called metal-cladding additives. The metal-plating lubricant assists to the realization of selective transfer as result of which a friction surface film is formed that is subjected to small oxidation. The film is formed of metal atoms introduced in the contact zone with the lubricant used, varying from several atom plies to 2 - 4 μm .

Metal plating lubricants are employed for heavy loaded friction couples in machines, airplanes, cars, etc. Their use doubles or triples durability, makes two times decrease of friction losses and lubricants costs, and promotes machine efficiency. Frequently applied are metal plating lubricants that form Cu, Sn and lead films on the frictional surfaces. The metal-plating additive application has been mostly realized in Russia, Germany and Poland, but also in other countries.

For example, metal mixture colloidum has been used in USA for a long time [24,31]. It decreases bearing friction and renews the worn out surfaces when added into lubricant. Adding colloidum into emulsion applied during metal cutting increases cutting speed and decreases wear of tool. Their mixture contains 70% copper, 30% lead, silver, tin and tellurium additives.

The use of copper-plated cast iron rings was suggested as a way of preventing "scuffing" in internal combustion engines and tests are described which support the practicability of this suggestion. The tests indicate that all the rings on a piston must be copper-plated to prevent rapid wear of the copper, should an unplated ring scuff the liner. Tests showed that piston ring copper coating made engine cylinder wear 500 times less [31].

Numerous publications report that, addition of powder copper and its alloys, silver, tungsten, cadmium, and other metals, molybdenum disulfides, polymers, etc. to lubricants has a favorable effect on friction processes. Metal-containing greases prepared by adding metal powders improve, in some cases, anticorrosion and wear-resistance properties, but they are not effective enough in the friction assemblies through which current is passed because they do not provide stable contact resistance. When these lubricants are used, operation of contacts is accompanied by sparking and noise. Besides, unstable contact resistance results in electrical erosion and, hence, reduced in wear resistance of contacting pairs [2, 29,30]. Many of the shortages are further avoided.

Works on developing friction units by analogy with living organism joints, so-called "intellectual" friction unit started were in progress in Russia [29]. As said, in a frictional contact appear self-organizing processes of nanoparticles alongside with servovite film formation (diffusion-vacancy shift mechanism, Rebinder's effect, electrophoresis, formation of coordination connections), i.e. processes and phenomena testifying a wear-free effect. Friction process will thus be transformed from a destructive into a creative one with reference to servovite film constant reproduction in the friction unit.

By testing, some efficient compositions have been developed [2,24,29,30]. For example, the repair-regeneration oil additives are new generation additives and have an important place in the application of lubricants. Added to oils or greases they assure partial regeneration of worn surfaces under special dynamic friction conditions. At the same time they decrease the moment of friction and the coefficient of friction in the contact pairs of machines. Different names were given to these additives, depending on their composition and condition. Most common are the organic oil-soluble additives. The hard non-soluble non-organic materials are habitually called antifriction additives, and composites based on polymers – modifiers.

The metal-plating composite additives are also named remetalizers. Their development is based on:

- the theory of system self-organization as per I. Prigogine, W. Ebeling, D.N. Garkunov, G. Polzer, etc. [1,7,8];
- the scientific discovery and the application of the selective transfer of materials between contacting surfaces and the no-wear effect originating with the work of D.N. Garkunov, I.V. Kragelskii, G. Polzer, V. Babel, P.Kornik, etc. [2,7,24,29,30].

Longevity of lubricant oil depends on the antioxidant property and the service properties during operation and storage. Influence of temperature and air oxygen assist oil aging, supposed it is not contaminated with wear debris. Hence lubricant oil antioxidation stability is most important for its service life. Less stability means also that it should be changed more often. During machine operation oil oxidation is intensified.

In order to reduce oil oxidation, metal-plating oil additives realizing selective transfer of materials were developed. One of the newest is the oil-soluble metal-plating additive "**Valena**". **Valentina Babel** used inorganic salts, halides, as oil additives for improving tribological properties of the surfaces. As metal halides are insoluble in mineral oil, organic compounds were used to dissolve salts and give stable compositions when combined with oil. Alcohols meet these requirements. Alcoholic solutions of metal halides were injected into the base oil obtaining lubricant compositions. The negative influence of their acidity could cause corrosive effect, so industrial anticorrosive additive were added into the compositions [2,29].

P. Kornik [30] outlines a newly developed and implemented in production method of machinery maintenance at a large industrial enterprise with the use of the patented antifriction metalplating lubricant additive “Valena” presenting research results on the application of tin-lead bronze in a selective transfer mode.

4. Illustrations

The phenomenon of direct coating deposition is assisted by the rubbing with deposition of brass under the special conditions of selective transfer of material [2,6-8]. An example of one of the manufactured devices, the MBZ 3A, is shown in Figure 2. In the contact zone forms brass frictional coat with special characteristics: improved tribological properties of the contacting surfaces, e.g. low wear at nonabrasive treatment of steel/cast iron, lower inclination for welding and seizure between the operating surfaces; possibility for dismantling-free restoration of worn units/couples, etc .



Figure 2 View of the brass-coating device MBZ 3A [7]

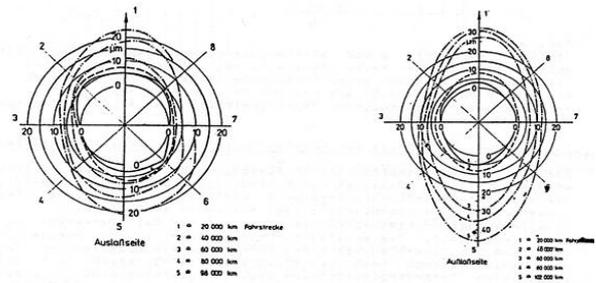


Figure 3 Wear distribution in upper dead point of engine cylinder after different sliding paths: for cylinder with frictional brass coating (left) and uncoated (right)

By means of brass frictional coating in different constructions of steel and cast iron, can be obtained not only the 10-20 % lowering of friction force, but also a changed wear distribution, which is to be seen, e.g., for the upper death point in engine cylinders of 2-cylinder- Otto-motors after various completed path lengths (see Figure 3).

Examples referring to the study of friction in ball bearings illustrate the influence of the presence frictional coatings and of “Valena” additive in the lubricant [7,9,18,19,21].

Experimental results of comparative studies with and without “Valena” additive in the lubricant have been obtained for the variation of lubricant temperature, friction moment, friction coefficient and wear were obtained in the Tribology Center at the Technical University – Sofia [9,21].

Illustration is given for the additive influence on the wear of cylindrical specimens of high strength cast iron micro-alloyed by various mass percent contents of tin (Sn) under lubricated conditions. Lubrication was provided with the transmission oil SAE 80W-90 without and with “Valena” additive [21].

Mass loss of the specimens has been measured after the given sliding time (0, 20, 30, 40, 50 and 60 minutes) in order to build the wear curves (Figures 4 and 5).

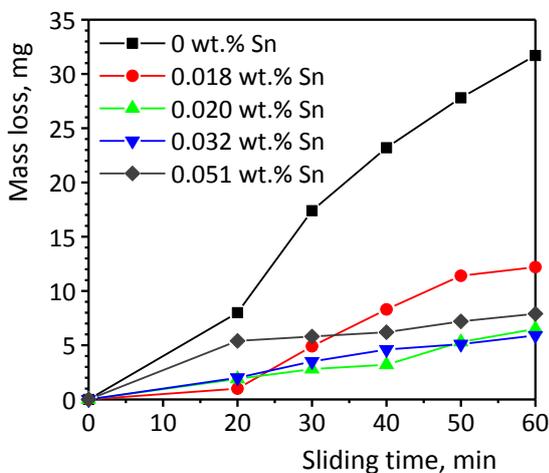


Figure 4 Wear curves; lubricant oil SAE 80W-90 without “Valena” additive

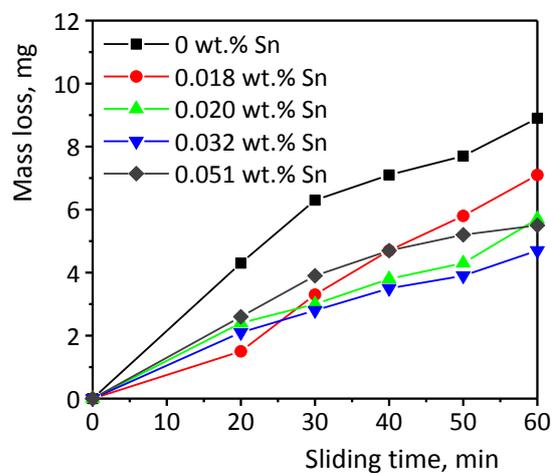


Figure 5 Wear curves; lubricant oil SAE 80W-90 with “Valena” additive

Wear curves of the tested materials showed that after initial period (running-in) the wear curves tends to stabilize, i.e. before the onset of the usually lower and linear steady-state wear, run-in wear appears as the initial high-rate transient wear. The wear values, for all specimens, were lower in the case of oil that contained “Valena” additive.

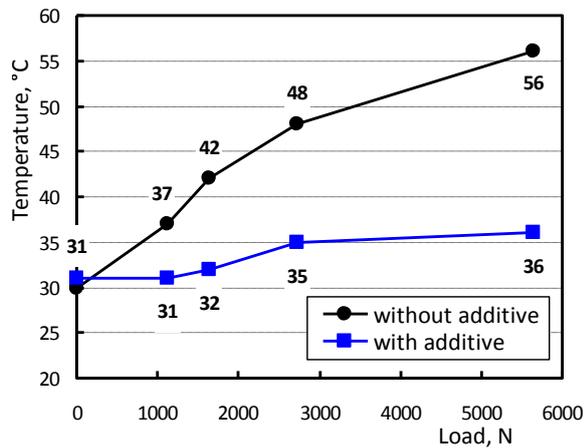


Figure 6 Variation of temperature of oil (with and without “Valena” additive) in bearing during friction with different loads

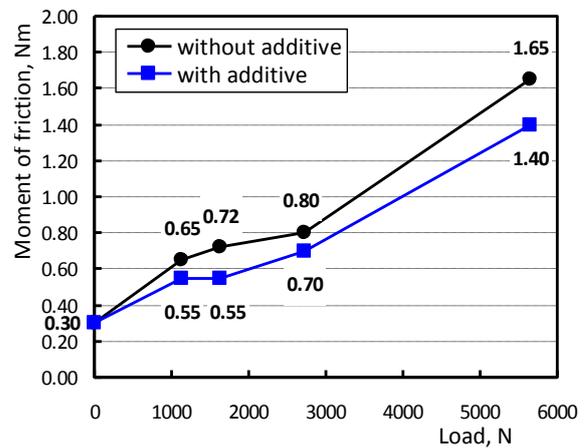


Figure 7 Moment of friction variation in bearing with different loads during friction for oil with and without “Valena” additive

The temperature of oil in the bearing junction, the friction moment and the friction coefficient in the case of oils with additive appear to be always lower than those by oils and greases without additives (Figures 6 and 7) [9].

5. Conclusion

The paper overviews the state-of-the-art in the investigations of the phenomenon of self-organization during selective transfer of materials in the contact of friction surfaces and the tribological processes that take place during friction under conditions of selective transfer. A basic one of tribology challenges: minimising the wear, is being discussed as wear reduction possibilities through frictional coatings.

Self-organization in the system brass-glycerol-steel under selective transfer is highlighted. It prevents dislocations accumulation in surface layers (unlike the case of boundary friction), a low shift resistance is obtained and a surface-active substance is formed which plasticize the metal. Hence, the obtained film – a designed or controllable coat with significant change of wear-resistance – can be intentionally manipulated to influence its properties during deposition in friction. The frictional coatings are eco-friendly as coat deposition (pollution-free technology) and as application through the improvement of the lifetime of friction units (energy and material saving by wear-reduction and by the dismantling-free restoration of worn units) [12,19,24,32].

An illustration of a modern development of lubricants and additive is done in the paper by the overview of the oil-soluble metal-plating composite additive “Valena” created and manufactured in Russia and Kazakhstan, and studied in the Tribology Laboratories of the Faculty of Industrial Engineering at the Technical University Sofia and the Faculty of Mechanical Engineering of Belgrade University.

The results have shown that the values of the tribological characteristics moment of friction, coefficient of friction and wear are for each load lower in the case of oil and grease that contain “Valena” additive. The results for oil temperature measurement confirmed that the decrease of moment friction and coefficient of friction in the case of oil with “Valena” additive is not due to oil viscosity reduction at higher temperature, but due to the physic-chemical surface effects in the contact region during friction.

Future successive tribological solutions will require significant research and development expenses. Engineering new materials, new coatings and new lubricants requires a considerable investment without a sure payout. Partnership between the big companies, the construction materials and lubricant producers and developers, with the researchers from universities and academies would be of great benefit. Moreover, the interdisciplinary character of the study and application of technologies for frictional coating formation, layer growth techniques, surface texturing, etc. involves intervention by specialists of different sciences. The work and collaboration between scientists of Russia, Germany, Poland, Bulgaria, Mongolia and Vietnam in this field was carried out by the International Council for Selective Transfer and Frictional coatings, established in 1990 in London.

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