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Some Aspects of Grease Flow in Lubrication Systems and Friction Nodes

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1. Introduction

An optimally designed lubrication system should reliably distribute a lubricant to particular reception points. The distribution must be precise and preferably fully automated. It is particularly difficult to design such a system if it is to supply a lubricant to heavily loaded machines, featuring a considerable (even up to a few hundred) number of different kinds of friction nodes distributed in a non-linear way, with long distances between each other. An additional problem might be hard conditions of the environment in which the system is expected to work (high or low temperature, high air humidity, etc.). All the conditions make the task of the designing of a reliable central lubrication system a real challenge, even for an experienced designer specialising in that particular field. While building a lubrication system it is important to define fundamental parameters which will determine its reliable operation. One of the crucial things is to select an appropriate grease that ought to reduce friction resistance and wear of the friction nodes, to protect them against the influence of the environment, as well as to guarantee the lowest possible flow resistance during its distribution (mainly through the lubricating conduits). An inappropriately selected grease, in terms of its rheological and tribological properties, and also the dynamically changing working conditions, may lead to a considerable increase in the operating costs of the machine.

The chapter contains the most important information on the structure of greases along with the discussion of the influence of the thickener's microstructure on the behaviour of the lubrication formula mainly in lubrication systems, but also in reception points, namely in the friction nodes (including roller bearings). It also refers to the problems of the influence of the mechanical stability of a thickener's microstructure on the quality of lubricating the roller bearings and their service life. Additionally, the chapter presents works on generating the lubrication film on the friction nodes working surface. Also, the fundamental problems

connected with the grease rheology (the grease performance in the fixed flow rate conditions and the notion of the linear and the non-linear viscoelasticity) have been discussed in the text. The state of the art knowledge on the fundamental phenomena observed in the lubrication systems, including the mechanisms of the thixotropic changes in the grease microstructure at shearing and relaxation, as well as the forming of the boundary layer at the grease flowing through the conduits in the main line of the lubrication system have been presented.

2. Microstructure of the lubricating greases

Lubricating greases are rheologically complex two-phase non-Newtonian fluids. They are chemically and physically heterogeneous. The dispersive phase is normally a mineral oil, a synthetic oil or a vegetable oil, whereas the dispersed phase is a thickener and, depending on the needs, solid additives. The particles of the thickeners can vary in their dimensions. Soaps, for instance, do not normally exceed 100 μm in length, and their diameter is not shorter than 0.1 μm and not longer than 0.5 μm [1-3]. The lithium and calcium soaps particles are definitely bigger than the sodium soaps particles. The isometric aggregates of bentonite clay and mica are approximately 0.5 μm in width and 0.1 μm in thickness [1]. The solid additives have similar dimensions. Due to the size of the thickener particles, the greases acquire the characteristics of the mechanically dispersed (suspension) or the colloidal system. The thickener particles size depends primarily on the process of the grease production [4,5], as well as on the conditions in the friction node. During the shearing of a grease in the friction node, the size of the particles can change considerably. According to Boner [5], in order to achieve the optimum tribological and rheological properties of a lubricating compound, greases containing variously dispersed thickener particles ought to be mixed. It concerns particularly the lubricants thickened with metal soaps. Too high particles dispersion of the thickener in the grease can negatively influence its lubricating properties. Such particles do not present enough capability of making spatial, three-dimensional structures resulting from the physicochemical interactions. Too long particles of the thickener cause too high an increase of the consistency of the lubricating grease and lead to its easy breaking both in the lubrication systems and the tribological pairs.

Microstructure of the lubricating greases with soap thickeners can be compared to a sponge with a lubricating oil (Figure 1). It makes a three-dimensional, coherent network of interconnected particles (flow units), in the literature referred to as *flocules*. The oil is locked in the free spaces of the microstructure through the mechanical occlusion, the capillary phenomena as well as the molecular attraction between the thickener and the polar components of oil [6]. It is estimated that the amount of the oil locked in the microstructure of the soap greases can amount even to 75%. The soap particles making the microstructure, from the chemical viewpoint, are associated molecules [7], namely groups of identical molecules generated as a result of the dipol-dipol type of interaction or the hydrogen bonds [8]. The final skeleton of the microstructure – shaped in the dispersion center – is made in situ in the process of crystallization of the soap particles and/or through nucleation, namely making crystallite nucleuses and their further growth [5]. The shape of the thickener particles and their surface topography can be different, depending on the kind of soap used and the particles' size. If they

exceed the size of 1 μm , their structure is rough and resembles twisted ropes. The crystallites of the colloidal size are definitely smoother and less twisted [3]. The microscope photographs also show a clear difference in the surface structure of the lithium, sodium and calcium thickener floccules [7,9]. The calcium soap particles are rougher than the particles of the lithium and sodium soaps, independently of their length [5]. In the case of the non-organic thickeners, the grease microstructure is made of numerous individual aggregates popularly called *open card-house* [10], for instance bentonite (Figure 2), mica or vermiculite. Such particles have a skeleton structure which resembles heterogeneous, fuzzy-edged, curled flakes or straight plates piled one on the top of the other [11].

The shape of the soap particles and other organic or non-organic thickeners, their anisometry (in reference to their length and lateral dimensions), as well as their dispersivity and the percentage in the full volume of the grease, greatly influence the physical properties of the ultimate lubricating compound [7,12-14]. The last two factors are critical for the easiness of the making of different energy connection types between the elements of the microstructure. Apart from providing the appropriate consistency, thickeners influence the way the lubricating grease flows, changes its shape or the type of flow resistance (pumpability) it presents. It is particularly important in the central lubrication systems where the lubricant is often transported in long conduits to particular receiving points.

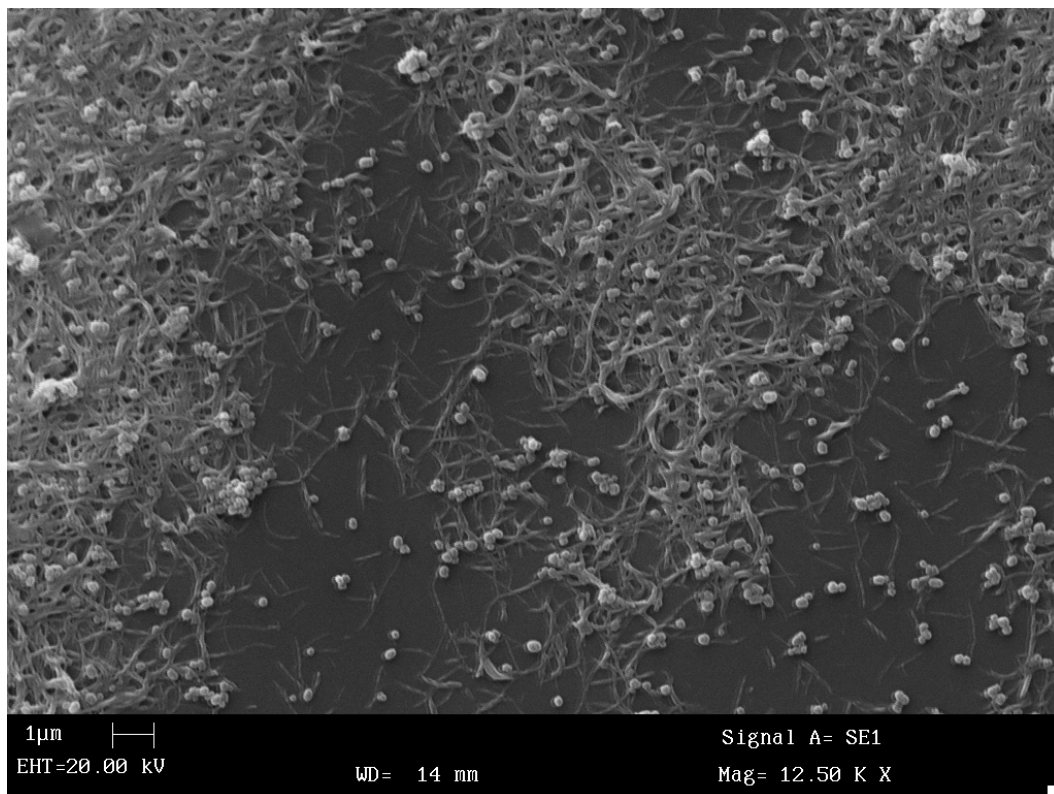


Figure 1. Floccules of the lithium thickener with particles of polytetrafluoroethylene (PTFE) improving the tribological properties of the lubricant. The microphotograph was taken by means of a scanning electron microscope (SEM) in secondary electron imaging (SEI) mode at the magnification of 12 500 times.

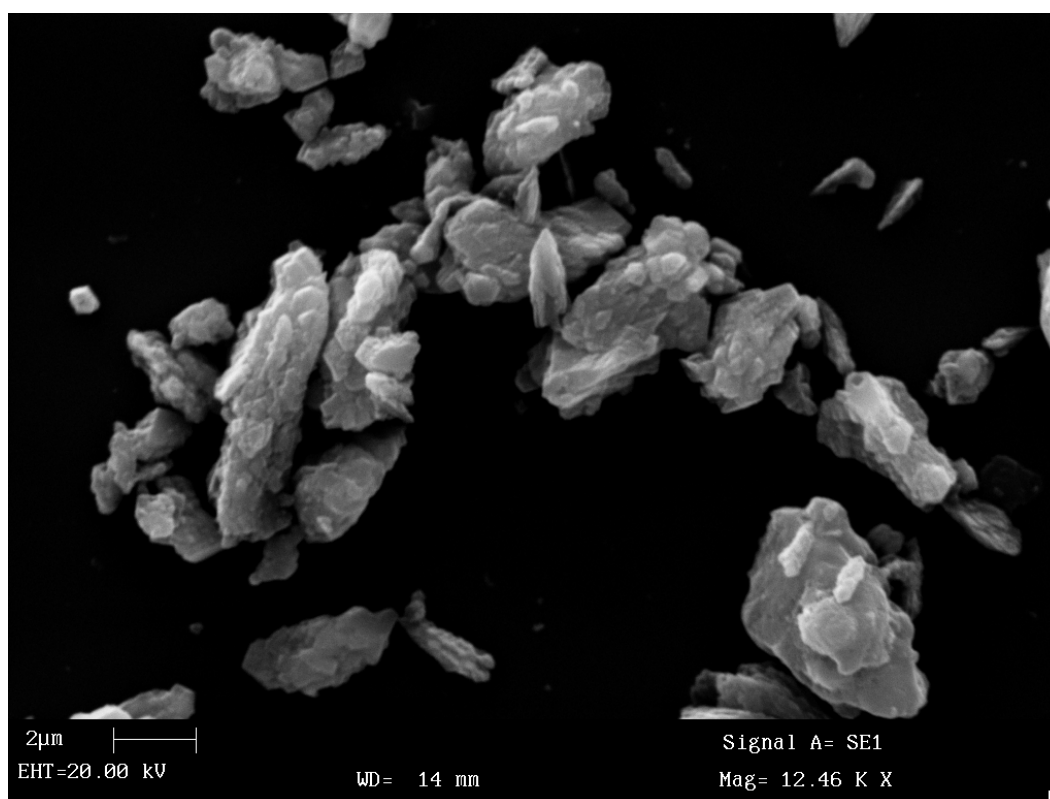


Figure 2. Bentonite clay aggregates making the *open card-house* structure. The microphotograph was taken by the scanning electron microscope (SEM) in secondary electron imaging (SEI) mode at the magnification of 12 000 times.

The mechanical durability and the stability of the microstructure of the thickener in a lubricating grease determines the friction reduction, the protection of the lubricated surfaces as well as the grease performance during the mechanical loading in the friction node and work at ultimately high temperatures. Cann [15] analyzed thin layers of the lithium lubricants without the solid additives on treadmill roller bearings with the use of attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy. The research showed that the oil gets out of the lubricated roller bearing as a result of damage in the thickener's microstructure. In the case of the untouched microstructure, the oil is connected with the thickener by means of the capillary forces. When the microstructure is damaged, it gets out of the bearing, washing out individual soap crystallites. Such an oil undergoes oxidation and evaporation easier, which lowers its lubrication quality. Additionally, its rheological properties are much worse than the properties of the base oil, and its kinematic viscosity is significantly reduced [16]. Similar conclusions were drawn by Farcas and Gafitanu [17]. Based on experimental research, Farcas and Gafitanu presented a mathematical model correlating the degree of the thickener microstructure destruction with the service life of the roller bearing. Their SEM photographs of the lubricating greases subjected to shearing in the roller bearing showed a damaged microstructure of the grease with the base oil bled out of it. According to the researchers, a crucial role in the process of the microstructure destruction is played by temperature. Above 60-70 °C, along with its increase by each 10-15 °C, the service life of the bearing falls by half. Above 70 °C, the bearing's failures are most frequently caused not by the contact fatigue, but predomi-

nantly by the degradation of the thickener's microstructure and worsening of the grease's properties. Vinogradov et al. proved that interactions between the thickener particles and the microstructure state may influence the increase of the friction moment in the roller bearing [18].

The thickener in the lubricating grease is responsible also for the thickness of the lubrication film on the working surfaces of the friction joints. Spikes, Cann, Wiliamson and Kendal in their works [19,20] presented results of the research on the interaction of the thickener's particles with the treadmill sprinkled with titanium oxide. They observed an increase in the thickness of the lubricating film in the elastohydrodynamic conditions of the collaboration of a steel ball with the treadmill. The measurement was done by means of Alström's method. In the case of the lubricants thickened with metal soaps, the biggest capability of making the lubrication film was recorded in the lithium grease. The thickness of the generated grease layer, apart from the kind of thickener, was also determined by the flow speed of the lubricant between the treadmill of the roller bearing and the rolling element. The thickness of the observed thickener's layer was 100 up to approximately 250 nm, depending on the kind of the lubricating grease. Long-lasting tests showed that the lubrication film's thickness generated on the bearing's treadmill, at a constant load, falls with time up to the stabilization at the level from 20 to 50 nm.

Apart from the thickener, the lubricating grease microstructure can also contain solid additives. Their main function is to improve the tribological properties of the lubricant. The solid additives are normally graphite, molybdenum disulfide (MoS_2), polytetrafluoroethylene (PTFE) as well as metal powders. The percentage of the solid additives in the grease usually does not exceed 5%. Research results indicate the benefits of the increase of the percentage of the solid additives in the lubricating greases. Of course, there are also works which show the advantages of the synergism of the powdered PTFE as well as tin and copper in the lubricating compounds [21,22].

Solid additives significantly influence the rheological properties of the lubrication compound [23,24]. The lubricants thickened with the polar lithium soap without the solid additives show quite high values of the structural viscosity and of the shear stress. After the enriching the lubricants with the graphite thickeners and MoS_2 the lowering of the parameters' values occurs. The additives reduce the shear stress both in the bulk of the grease as well as in the boundary layer. Research show that PTFE does not influence the change of the values of the parameters in the lithium soap. In the case of the lubricants thickened with the bentonite clay, solid additives cause the increase of the yield stress both close to the wall and in the bulk of the grease. The most influential determinant of the values increase is the graphite thickener. Adding the PTFE in this case does not significantly determine the structural changes thus generated lubrication compound.

3. The basic rheological properties of the lubricating greases

3.1. Behaviour of the lubricating greases in the steady flow conditions

Greases, depending on their characteristic structure, are shear-thinning (pseudoplastic) and rheunstable fluids having a yield point. They show very complex rheological properties.

Lubricating greases, at very low shear rates behave like a Newtonian fluid of a constant viscosity η_0 , being a slope of a tangent to the flow curve, equal to the shear rate going to zero ($\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma})$). At the shear rate going to infinity, lubricating greases also behave like Newtonian fluids, but of viscosity η_∞ close to the dispersion phase, namely of the base oil ($\eta_\infty = \lim_{\dot{\gamma} \rightarrow \infty} \eta(\dot{\gamma})$). The viscosity η_∞ is a slope of a straight line being a flow curve asymptote. In the bracket of the indirect shear rates, the curve of the lubricating grease flow curve is described with the following equation:

$$\eta = \frac{\tau}{\dot{\gamma}}, \quad (1)$$

where: η - dynamic viscosity, τ - shear stress, $\dot{\gamma}$ - shear rate.

Figure 3 illustrates results of the rheological measurements made on the lithium greases of a various thickener percentage, showing the shear stress changes and of the structural viscosity as a function of the shear rate. Additionally, the theoretical curves generated from the Herschel-Bulkley's [25] and Carreau-Yasuda's [26] dependences have been presented. Values of the parameters defining the theoretical curves traced according to the abovementioned dependences for the greases of a various thickener percentage have been presented in Table 1. The greases were thickened with lithium 12-hydroxystearate, and the oil base was ORLEN OIL SN-400 (ORLEN OIL, Cracow, Poland) mineral oil. The flow curves were defined at temperature of 25 °C. The tests were repeated five times, and their results were statistically elaborated at the confidence level $p = 0.95$, using t-Student test. Additionally, correlation coefficient values were calculated. The experiment was carried out by means of Physica Anton-Paar MCR 101 rotational rheometer. The rheometer was working in the cone-and-plate system (CP-25-1, 25 mm, 1°) at a constant measuring gap height of 49 μm .

Thickener content (%)	Herschel-Bulkley model				Carreau-Yasuda model					
	τ (Pa)	k_c (Pas)	m	R_{xy}	$\eta_0 - \eta_\infty$ (Pas)	η_∞ (Pas)	λ (s)	a	n	R_{xy}
4.0	120.27	5.826	0.66964	0.99983	1852.4	0.38843	47.456	2	0.20073	0.99600
5.0	190.52	83.155	0.37458	0.99958	4189.5	0.20014	47.457	2	0.23465	0.99668
6.0	216.00	83.867	0.38633	0.99973	4742.5	0.26093	47.939	2	0.22985	0.99811
6.5	241.47	212.430	0.29112	0.99982	9090.5	0.18576	47.940	2	0.20100	0.99919
7.0	672.60	148.930	0.35189	0.99750	15225.0	0.26328	47.455	2	0.17468	0.99696
8.0	712.54	285.550	0.28687	0.99592	21453.0	0.25487	47.423	2	0.16048	0.99944
9.0	785.29	230.630	0.37532	0.99956	16023.0	0.54032	47.458	2	0.21285	0.99743

Table 1. Values of the parameters determining the theoretical curves traces, defined according to dependences (1) and (2) for the greases of the thickener content 4-9%.

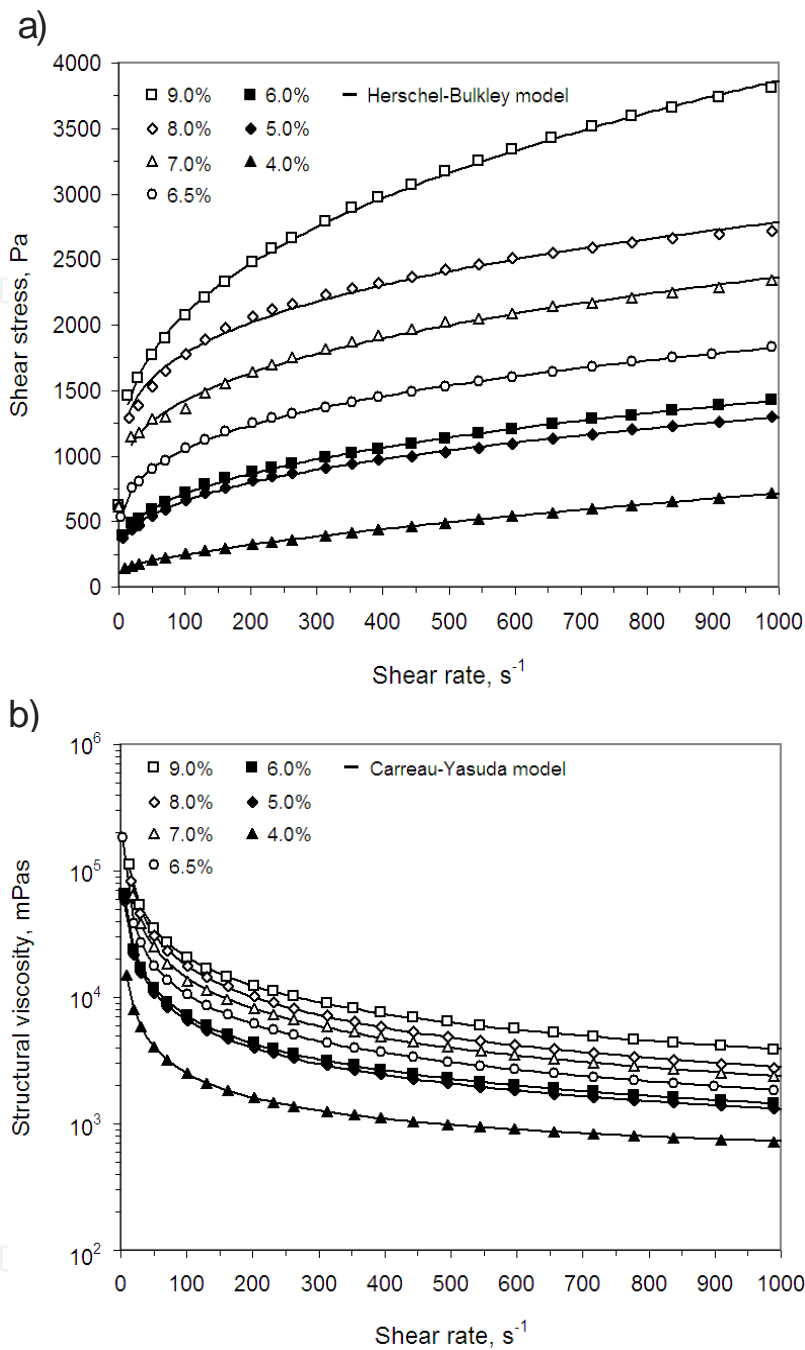


Figure 3. Dependences of the shear stress (a) and the structural viscosity (b) in a function of the shear rate for the lithium greases based on the mineral oil, with a various thickener percentage. The diagrams, in order to achieve a greater clarity, do not contain the confidence intervals.

The Herschel-Bulkley (2) dependence takes into account the existence of a yield stress τ_0 value, namely such a value of the shear stress above which the lubricating grease starts flowing:

$$\tau = \tau_0 + (k_C \cdot \dot{\gamma})^{\frac{1}{m}}, \quad (2)$$

where: τ_0 – yield stress, k_C – consistency factor of the thickener in the grease, m – nondimensional index exponent. Carreau-Yasuda (3) dependence enables approximation of the course of changes in the structural viscosity as a function of the shear rate with viscosity η_∞ and η_0 included:

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty) \cdot [1 + (\lambda \cdot \dot{\gamma})^a]^{\frac{n-1}{a}}, \quad (3)$$

where: $\eta_\infty = \lim_{\dot{\gamma} \rightarrow \infty} \eta(\dot{\gamma})$, $\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma})$, λ – time-constant, a and n – nondimensional parameters. For the shear-thinning fluids, a parameter normally equals 2 [27].

The flow curves clearly illustrate the fact that the greases have the pseudoplastic properties. It results from the degradation of the lubricating greases' microstructure as well as from the further orientation of the dispersed particles of the thickener. During relaxation of the stress in the lubricating grease, a considerable entanglement of the thickener particles is observed. However, during shearing of the grease, one can record straightening and untangling of the particles which are directed along the current line. With the increase of the shear rate, the effect is more and more visible. The reduction of the internal friction resulting from a smaller size of the particles and a limited activity between them is observed. At very high shear rates, the total orientation of the particles in the grease is achieved. The internal friction remains constant at a low level. The structural viscosity of the grease then gets close to the viscosity of the base oil.

Figure 3 shows that at a large enough percentage of the dispersion, the interaction between the thickener particles may cause formation of the spatial microstructure resistant to the shear stress which does not exceed certain value. Below the value, the lubricating grease behaves like an elastic solid. When yield stress τ_0 (yield point) is reached, the microstructure gets damaged and the grease starts behaving as a viscous liquid. When the shear stress in lubricating grease becomes lower than the limit value, the immediate reconstruction of the microstructure takes place. The determination of the yield stress value in the lubricating grease is very important because it enables the determining of its usefulness for the application in the central lubrication systems of machines [9,28] or in the friction nodes [7].

3.2. Linear and non-linear viscoelasticity

When a lubricating grease undergoes the periodic stress oscillation, its response in a form of a relative deformation will be shifted in the phase by δ angle. The angle, called the phase angle shift, falls in the range from 0° to 90° . The response of the lubricating grease determined by the extortion is influenced primarily by: complex modulus $|G^*|$ and complex viscosity $|\eta^*|$. The complex modulus is defined as a sum of the real and the imaginary part:

$$|G^*| = G' + iG'', \quad (4)$$

where: G' - storage modulus (elastic component in the phase with the stress), G'' - loss modulus (viscous component shifted in the phase in relation to the stress). Components G' , G'' are equal:

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta, \quad (5)$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta. \quad (6)$$

Storage modulus G' is a measure of the energy stored and recovered per each deformation cycle, whereas loss modulus G'' is a measure of the energy lost per a sinusoidal deformation cycle. What results from equations (5) and (6) is that phase angle shift δ can be defined as:

$$\tan \delta = \frac{G''}{G'}. \quad (7)$$

The dispersion effects can also be described by means of complex viscosity η^* . The complex viscosity, similarly to the complex modulus can be formulated as:

$$|\eta^*| = \eta' - i\eta'', \quad (8)$$

where:

$$\eta' = \frac{G_0}{\gamma_0 \omega} \sin \delta, \quad (9)$$

$$\eta'' = \frac{G_0}{\gamma_0 \omega} \cos \delta. \quad (10)$$

The real part of complex viscosity η' is called the viscous component or, less frequently, the dynamic viscosity, whereas imaginary part η'' is called the elastic component. The measurement of quantities G' , G'' and η' , η'' enables the rheological characteristics of the greases in terms of their viscoelastic properties.

Figure 4 illustrates example results of a strain sweep test of Nanolubricant 2010 (Orapi, Saint-Vulbas, France) commercialgrease, thickened with the lithium 12-hydroxystearate, based on

a synthetic oil with the addition of tungsten disulfide nanoparticles. The deformation range of the grease was 0 to 100% at 1 Hz oscillation frequency. The measurements were done at 25 °C. The oscillation measurements made it possible to determine the limit of the linear viscoelasticity (marked in the diagram with the vertical line). The research showed that plateau modulus G_N^0 for Nanolubricant 2010 was 75 743 Pa at deformation γ_C equal 0.336%. The review of the methods used for the determining of the linear viscoelasticity limit (the critical point) on the basis of the dynamic-oscillation tests is widely discussed in [29].

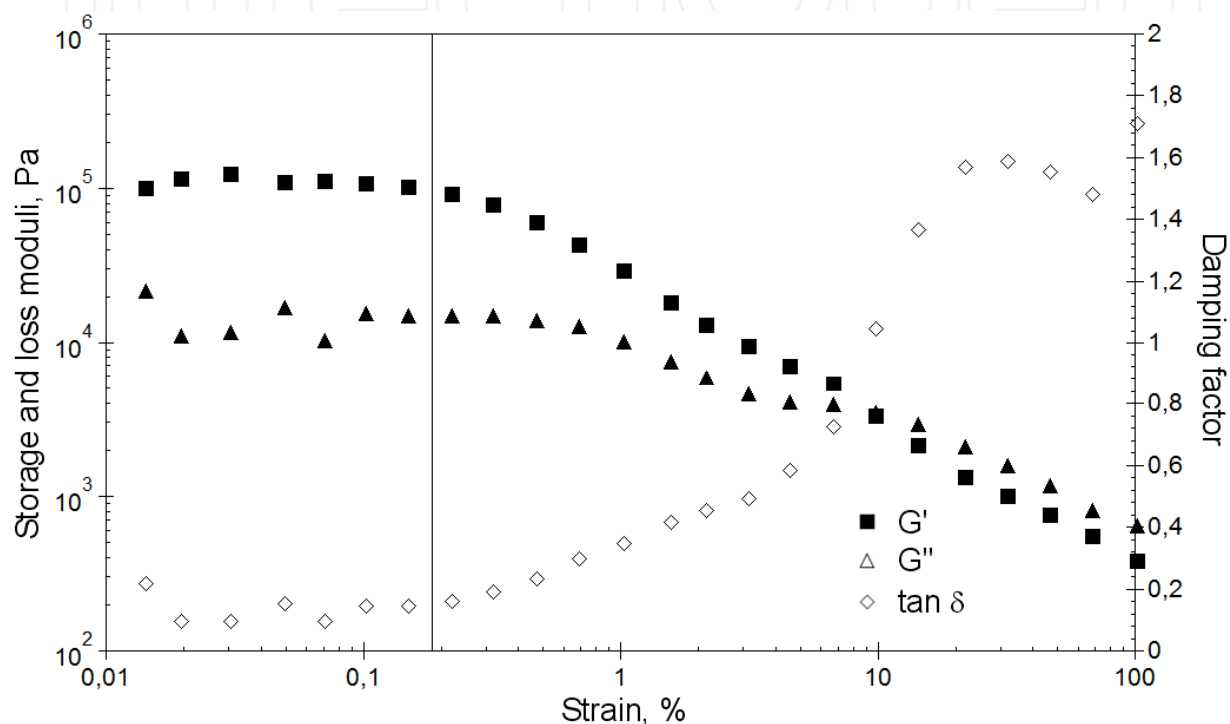


Figure 4. The storage and loss moduli and the phase angle shifts as a function of Nanolubricant 2010 grease strain.

Figure 5 illustrates the influence of the soap thickener (lithium 12-hydroxystearate) percentage in the lubricating grease based on the mineral oil on (a) value of critical strain γ_C and (b) of shear stress τ in the critical point, as a function of the percentage of the thickener. The diagrams show that the range of the linear viscoelasticity depends on the percentage of the thickener in the grease – the smaller percentage of the thickener, the wider range of the linear viscoelasticity. In the case of the shear stress in the critical point, there is an adverse situation. The research was carried out by means of a stress/strain controlled rotational rheometer Physica Anton-Paar MCR 101. The rheometer was working in the cone-and-plate system (CP-25-1, 25 mm, 1°) at a constant measuring gap of 49 μm .

The rheological dynamic-oscillation research (which is a combination of the creep and relaxation experiments) are currently the basic tool at evaluating the structure of dispersion and its mechanical stability as well as the behaviour of the lubricating grease in the start phase of the flow. At high frequencies and amplitudes, the dynamic-oscillation tests can be used for the determining of the speed at which the microstructure is created and damaged under the

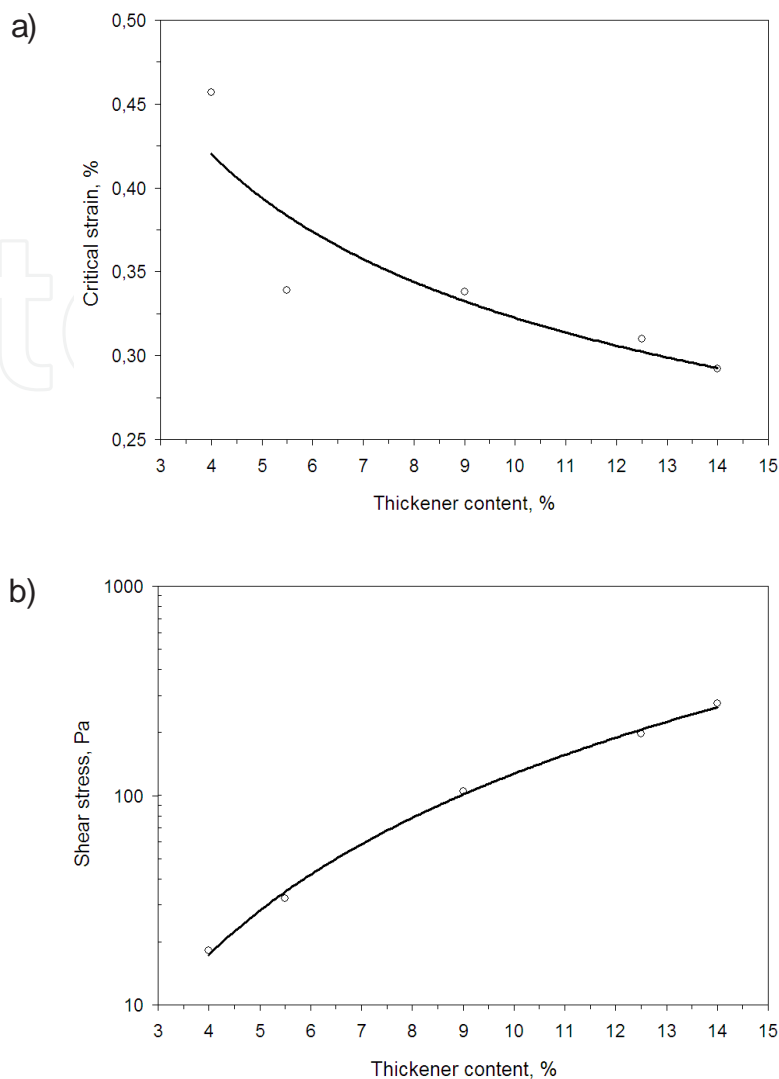


Figure 5. Critical strain γ_c (a) and shear stress τ in the critical point (b), as a function of the percentage of the lithium thickener in the lubricating grease

influence of oscillation. Carrying out such research is important for the evaluation of the lubricating greases' behaviour at the start-up phase of the friction nodes and of the flow in the lubrication systems conduits. The dynamic-oscillation research on the lubricating greases has been, among others, conducted by Yeong et al. [14] as well as Delgado [12], Martín-Alfonso et al. [30,31].

4. Mechanism of thixotropic changes in the microstructure of the lubricating grease during its shearing and relaxation

The term 'thixotropy' comes from the Greek words *thixis* (mix, shake) and *trepo* (revolve, change), and it was first suggested by Péterfi [32] (the original name – *thixitropy*) [33]. The

phenomenon is defined as an isothermal decrease in structural viscosity during shearing followed by an increase in the viscosity and the re-solidification of the substance once shearing ends [34]. The phenomenon of thixotropy concerns suspensions of the internal microstructure made of particles which undergo aggregation or flocculation. In such systems, there are physical interactions between particles, which, during relaxation of a substance, determine the creation of a spatial, cross-linked microstructure. They are primarily the Van der Waals-London attractive forces, the electrostatic repulsive forces (particularly important when the dispersed phase particles are anisometric in shape) as well as the steric forces. Also, the Brownian motion may have an important part to play in the process, but their appearance is limited only to colloids. A wide description of the intermolecular interactions which are common in thixotropic systems can be found in the publications of Efremov et al. [35,36] as well as of Sonntag's [37] and Scheludko's [38]. During shearing, the microstructure made of the dispersed phase particles, as a consequence of their mutual interaction, gets disintegrated forming bigger aggregates and individual particles, floccules, suspended freely in the dispersion medium. The review of the references concerning the thixotropy of suspensions can be found, for instance, in the publications of Mewis and Barnes [10,39].

The lubricating greases also show thixotropy. The structural viscosity of the lubricating grease decreases systematically during its shearing in the tribological node or during its flow through lubrication system conduits. The standstill of the grease leads to its re-solidification and a little increase in its structural viscosity. The decrease of viscosity during flowing of the grease is reduced to a certain minimum value, primarily depending on the viscosity of the base oil, a kind and amount of the thickener as well as the shear rate. At high shear rates, the structural viscosity of the grease reaches the value close to the base oil viscosity. According to Czarny [1] "Both in the slide bearings and in the roller bearings, the high-speed ones in particular, the rheological properties of the lubricant, so its hydrodynamic lift force, are determined mainly by the base oil. The thickener influences the force at the start-up and at the stopping of the bearing." Due to the complexity of the processes of degradation and reconstruction of the thickener's microstructure in the lubricating greases, scientific works which would thoroughly explain the processes have not been published so far.

The first publications on thixotropy of the lubricating greases appeared at the beginning of the 1950s. In 1951, Moore and Cravath published their work [13] on the mechanical process of the soap fibre disruption in the lubricating greases caused by the shearing force and on the influence of the disruption on the change of the consistency of the greases. The research concerned the lubricants thickened with the barium, sodium, lithium and calcium soaps. The degradation of the soap fibre consisted in the working of the samples in a penetration apparatus, as well as on their long-lasting disintegration in a rolling apparatus. During shearing, at different intervals, the measuring of the greases micropenetration level was performed. The tests showed that the biggest differences in the consistency of the greases were observed in the commercial grease thickened with the barium soap, whereas the smallest differences were recorded for the lithium grease. Additionally, a series of photographs of single soap fibres by means of an electron microscope was taken. The photographs showed a considerable difference in the fibre length before and after shearing for most of the tested samples. Moore and

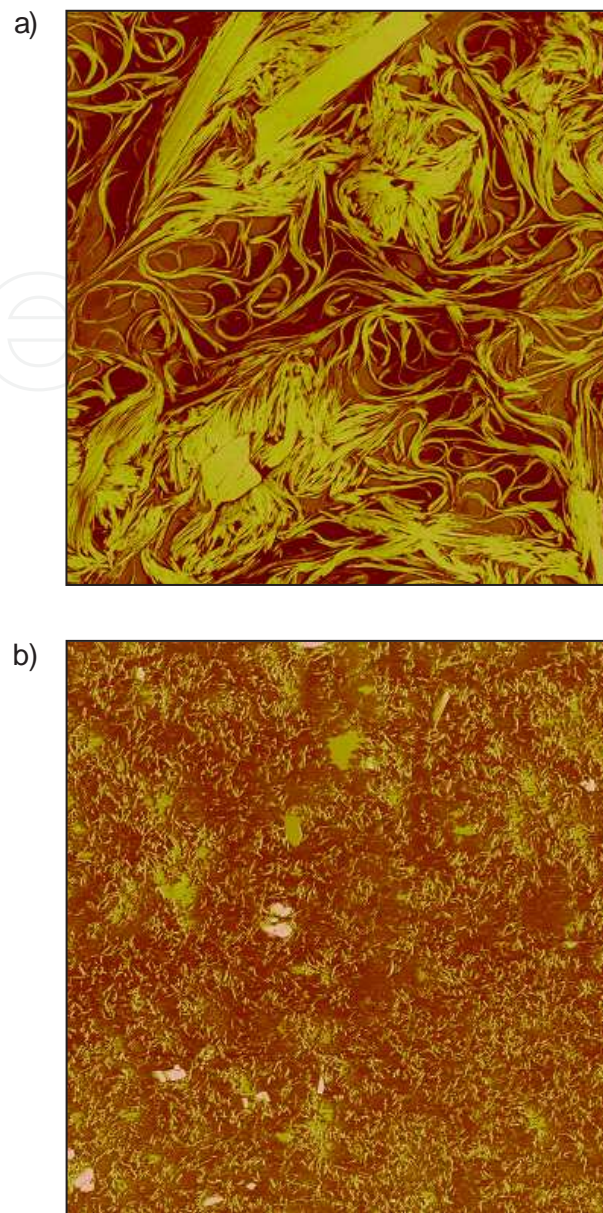


Figure 6. Microstructure of the lithium thickener in the paraffin oil [40]: (a) fresh grease, (b) grease sheared at 120 °C for 10 hours at $\dot{\gamma} = 0.01 \text{ s}^{-1}$ shear rate. The microphotograph taken by means of the atomic force microscope (AFM). Scanning area 20 $\mu\text{m} \times 20 \mu\text{m}$.

Cravath proposed a soap fibre disruption intensity model at different times of the external shearing force activity.

A similar analysis to the one conducted by Moore and Cravath was carried out by Renshaw [41]. He was particularly interested in the lithium thickened greases based on the ester oil, which showed high shear resistance. The measuring of the micropenetration was done directly before and after the 9-hour long shearing of the grease in a bearing at the speed of 10 000 rev/min and after 100 000 double strokes of the piston in the penetration apparatus. In the first case, Renshaw observed in the electron microscope, a considerable shortening of the lithium

thickener's fibre and slight changes in the micropenetration values. After the working of the grease in the penetration apparatus, the situation was exactly reverse, namely the changes in the micropenetration were remarkable but the particles were shortened only to a minor extent. The research showed that the intensity of degradation in the thickener's microstructure depends not only on the mechanical strength of individual fibres, but mainly on the shearing way and on the direction of the fibres at the flow of the grease.

Sirianni et al. [42] investigated the question of the influence of size of the calcium and barium soaps and their concentration on the change of the lubricating greases *thixotropy coefficient*. For the experiment, they used a theory proposed earlier by Goodeve and Whitfield [43] which was aimed at the determination of the thixotropy of the black suspension in the mineral oil [44]. According to the theory, the speed of the microstructure reconstruction (proportional to the thickener's concentration) equals the speed of its degradation. The thickener's concentration, however, is proportional to the difference between apparent viscosity η and grease equilibrium viscosity η_0 following the total degradation of the cross-linked microstructure of the thickener at the infinitely high shear rate.

$$\eta - \eta_0 = \frac{\theta}{\dot{\gamma}} = \frac{F_T}{\dot{\gamma}}, \quad (11)$$

where: η – apparent viscosity, η_0 – equilibrium viscosity, $\dot{\gamma}$ – shear rate, θ – thixotropy coefficient, F_T – momentum generated by the intermolecular forces transmitted by the unit of surface in the unit of time.

The theory assumes that at the increase of $1/\dot{\gamma}$ expression, apparent viscosity η rises until it reaches the plateau. According to Goodeve and Whitfield, the thixotropy coefficient is a source of the non-Newtonian effects, which is directly correlated with the intermolecular bonds disruption effects, the average life span of the bonds and the change of size of the interacting molecules in the thixotropic process. In order to calculate the thixotropy coefficient, Goodeve assumed that the bonds between the molecules of the dispersed phase are subject to Hooke's law.

Moses and Puddington [45], using the same theory, determined the influence of the thickener's percentage (10%, 14% and 19.7%), the shear rate (from 1 400 s⁻¹ to 250 000 s⁻¹), temperature (from 35 °C up to the value at which a visible sedimentation occurs) as well as the size-reduction of the thickener particles, on the change of the *thixotropy coefficient* of the lithium, sodium and aluminium greases. Different sizes of the soap fibre were generated by means of the colloid mill. For determining equilibrium viscosity η_0 a metal capillary was used.

Hahn, Ree and Eyring [46], while observing behaviour of the macromolecular polymers suspensions, formulated a theory (later called *sinh law*) which ultimately was widely used for the quantity description of the phenomena of the lubricating greases microstructure degradation and reconstruction, where the soap is a thickener. They took into account the fact that the thickener's structure contains the so called entangled particles (aggregates which create a three-

dimensional network and make the solution acquire the non-Newtonian fluid properties) and the not entangled particles (single floccules which make the solution acquire the Newtonian fluid properties). The number of the former and the latter depends on the temporary shear stress. The flow curve equation used by Hahn et al. was:

$$\tau = \frac{\chi_1 \beta_1}{\alpha_1} \dot{\gamma} + \frac{\chi_2}{\alpha_2} \sinh^{-1}(\beta_2 \dot{\gamma}), \quad (12)$$

where: χ_1 – share of the not entangled particles, χ_2 – share of the entangled particles, $1/\alpha_1$ – the not entangled particles shear stress, $1/\alpha_2$ – the entangled particles shear stress, $1/\beta_1$ – shear intensity for the not entangled particles, $1/\beta_2$ – shear intensity for the entangled particles, $\dot{\gamma}$ – shear rate.

Hahn and the collaborators assumed that at the increase, and next at the decrease of the shear rate, the free energy of the soap particles changes, and it is directly dependent on their strain energy. The cross-linked particles aggregates featuring the non-Newtonian characteristics get untangled making individual floccules, freely suspended in the dispersion medium, featuring the Newtonian characteristics. The process is reversible. Two years later, the scientists presented the equation of the changes kinetics [47]:

$$-\frac{d\chi_2}{dt} = \chi_2 k_f e^{\frac{\eta_0 w^2}{kT}} - \chi_1 k_b e^{\frac{-(1-\eta_0)(w')^2}{kT}}, \quad (13)$$

where: k_f – parameter determining the time of the entangled particles → not entangled particles reaction; k_b – parameter determining the time of the not entangled → entangled particles; w – elastic strain energy of the entangled particles, w' – elastic strain energy of the not entangled particles, η_0 – viscosity of the entire thixotropy system at zero shear rate, k – Boltzman constant, T – temperature.

Thus, Hahn et al. elaborated theoretical flow curves for the lubricating greases during the disruption and reinforcenment of the thickener's structure. The models have been widely applied for the determination of the thixotropic properties of, for instance, motor oils [48]. Validity of the assumptions made at the making of the mathematical dependences was proven by the experimentally developed curves. The mathematical model proposed by Hahn was also used by Utsugi et al. [49]. They analyzed the thixotropy of the calcium greases and the silica gel thickened greases. At the determining of the thixotropic hysteresis loop, Utsugi used the rotational rheometer. Bair [50] proved that the models proposed in the 1960s by Hahn and Eyring were still true. During the verification of the models, Bair used more technologically advanced rotational rheometers. He drew particular attention to the possibility of the dependences application for describing the thixotropy phenomenon of the lubricants working at the friction contact, in the elasto hydrodynamic conditions.

Vinogradov, Deinega and Verbitsky [18] investigated the correlation between the changes of the friction momentum in the ball bearings and the thixotropic properties of the calcium and the lithium greases. At the research, they observed that the shape of the dispersed phase particles considerably influences the behaviour of the lubricating greases during their further deformation and shear-thinning. On the turn of the 1960s and 1970s, Vinogradov also investigated the lubricating greases using the polarimetry and other optical methods. It enabled the quantity evaluation of the level of the thickener microstructure reconstruction. He also conducted research on the thixotropic hysteresis loop for the calcium and lithium greases with the use of the rotational coaxial cylinder rheometers. His works are widely discussed by Froischteter in [7].

Sacchetti, Magnin, Piau and Pierrard [51] published in the Journal of Theoretical and Applied Mechanics a paper on the thixotropic properties of commercial greases: Shell Alvania, ELF Multi and ELF EL series (8305-8308 and 9309) of NLGI (National Lubricating Grease Institute) 2 consistency class. The analyzed lubricating greases showed a different fibre length of the soap thickener (lithium 12-hydroxystearate). The oil base in the greases was the mineral oil. Sacchetti et al. focused mainly on the research of change in the shear stress as a function of shearing time. They analyzed changes in the lithium thickener microstructure at the cyclic shearing lasting a few seconds at different shear rates (from 0.018 s^{-1} to 18 s^{-1}) and different grease relaxation time (from 2 minutes to 38 hours). They did not analyze the structural viscosity increase of the greases at their relaxation, however. Apart from the thixotropy, Sacchetti et al. investigated the wall effects.

Czarny, in his paper [52], presented results of the research on the process of degradation and reconstruction of the thickener microstructure in the commercial calcium greases (STP) and the lithium greases (LT-4S2). He used the method of cyclic shearing of the lubricating grease at specified time intervals, at a constant shear rate. The research on the grease was carried out without removing it from the rheometer head. He thus simulated the conditions observed in the conduits of lubrication system. In 1990, Czarny investigated the influence of temperature on the thixotropy of the lubricating greases [53]. He proposed a mathematical description of the energetic changes which take place in the microstructure of the thickener during its shearing at various temperatures. Czarny observed that along with the temperature increase, the structural viscosity of the lubricating grease is reduced, and the activity of the thickener particles increases. According to Czarny, the motion of the particles along with the increase in the lubricant temperature, a certain energetic barrier, which Czarny called *the activation energy*, must be overcome. Czarny also carried out the research on the degradation of the thickener microstructure by means of the Couette rotational rheometer, and on the influence of temperature on the process. He investigated the bentonite greases, the calcium greases (STP, Kalton EP1), the lithium greases (Shell Alvania EP2, LT4-S2) as well as the lithium-calcium greases. In accordance with the experimental research and the theory proposed by Czarny, when temperature increases, the thickener intermolecular bonds get weakened, making a cross-linked, compact microstructure, and the activity of single crystallites freely suspended in the base oil increases. As a result, the lubricating greases, in the process of long-lasting shearing, take on the Newtonian fluid characteristics.

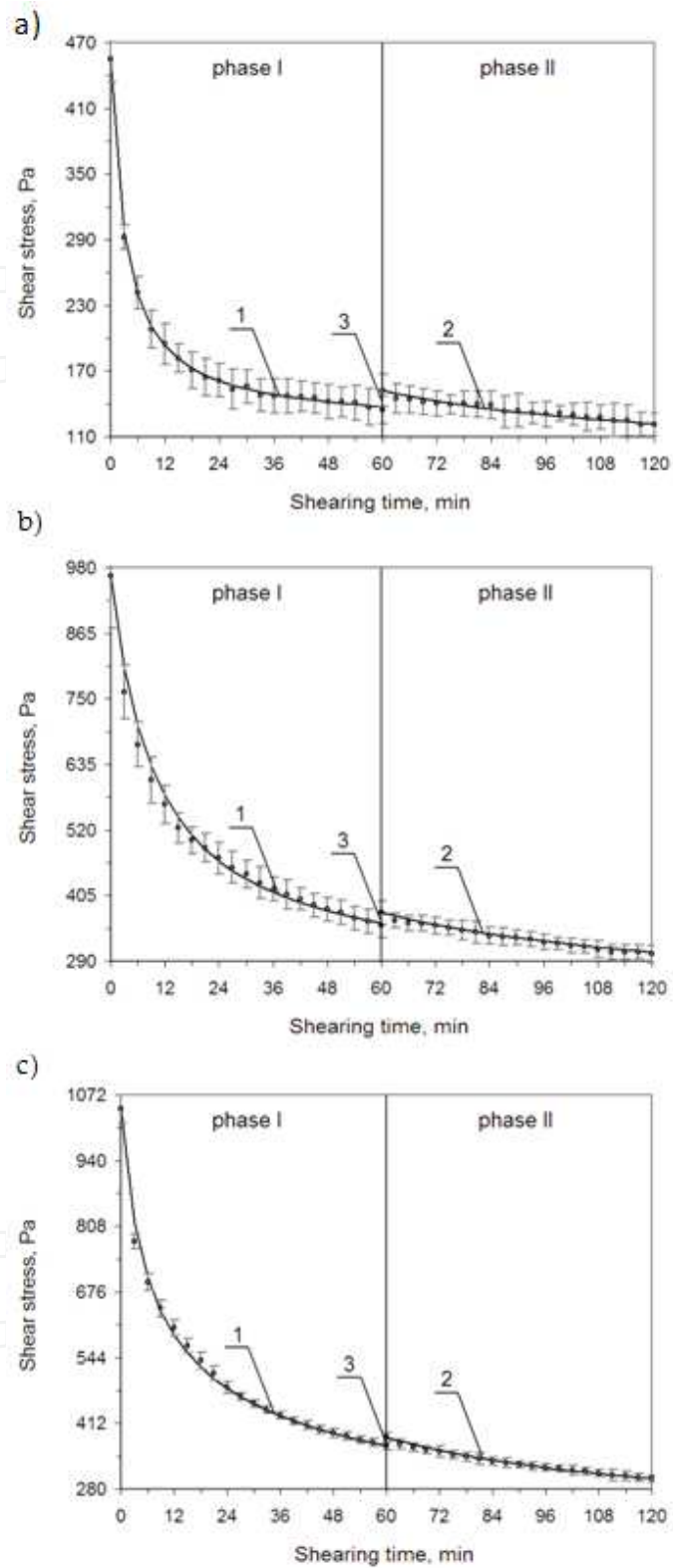


Figure 7. Dependence of the shear stress as a function of shearing time at constant shear rate $\dot{\gamma} = 8.1 \text{ s}^{-1}$ ($p = 0.95$) for the greases with the thickener percentage: (a) 6%, (b) 7%, (c) 8%. 1 – the first stage of shearing, 2 – the second stage of shearing, 3 – resolidification process of the grease in its relaxation phase.

Figure 7 illustrates the thixotropy curves for the lubricating greases thickened with the lithium 12-hydroxystearate based on the mineral oil, received by means of the measuring method proposed by Czarny. The grease shearing time in two cycles was 120 minutes in total. The grease relaxation time between the shearing cycles was 24 hours. The research was repeated five times. The experiment was carried out with the use of Rheotest 2.1 rotational coaxial cylinder rheometer working at 2 mm measuring gap. For the measurements, a right handed helix shaped grooved polytetrafluoroethylene internal cylinder, with 95 0.5 mm-deep grooves was used. Such a surface structure enabled a visible reduction of the Weissenberg effect and of the slip effect at the cylinder wall, which could have negatively influenced the measurements.

The energetic interpretation of the lubricating greases thixotropy was presented by Kuhn [54]. He focused primarily on those cases of thixotropy of the lubricating greases which occur during the hydrodynamic lubrication of the slide bearing. According to Kuhn, the energy loss during the friction shearing of the grease is a function of the lubricant's qualities and the conditions it is sheared in. If the lubricant's qualities change in the process of the fluid friction, *the energy density* (energy/volume) also changes:

$$e_{rh_e} = \eta \dot{\gamma} \left(\frac{\bar{d}_e}{h_0^*} \right), \quad (14)$$

where: e_{rh_e} – rheological density of energy in the microcontact region (J/mm^3), η – dynamic viscosity (Pas), $\dot{\gamma}$ – shear rate (s^{-1}), \bar{d}_e – average diameter of the microcontact (mm), h_0^* – average lubrication film thickness (mm).

Using the dependence presented above, Kuhn estimated friction coefficient μ which was:

$$\mu = \frac{e_{rh}}{p_r} i_{rh}, \quad (15)$$

where: e_{rh} – sum of the rheological energy densities in the region of all microcontacts (J/mm^3), i_{rh} – friction intensity (non-dimensional value), p_r – pressure (MPa).

Kuhn also observed a similarity between the curve of changes in the rheological energy density as a function of time at different shear rates and the curves received by Czarny [55] on the experimental way. Later in his work, Kuhn developed the energetic model of the lubricating greases thixotropy [56,57], and together with Balan suggested the experimental ways of estimating the rheological density of energy with the use of the rotational cone-and-plate rheometer [58]. In [59], he defined the tribological properties of the lithium and calcium greases based on the mineral oil by means of the energetic parameters, and also presented the relations between the viscoelastic properties of the lubricating grease, the friction in the frictional contact and the elastic strain energy accumulation and the shear stress at the shearing of the grease.

Kuhn's research proved that in the quantification of the tribological processes, the energy loss resulting from the structural changes which take place in the frictional contact region must be taken into account.

5. The rheological properties of the boundary layer in the lubricating greases

Lubricating greases are, on the one hand, required the best possible slide and anti-corrosion properties, and on the other hand, the lowest possible and independent of conditions flow resistance at the supplying of the friction nodes. The problem of the flow resistance of the lubricating greases is currently particularly important in the context of lubrication systems. It results primarily from the fact of a higher and higher automation of the systems. The flow resistance have negative influence on the proper functioning of the central lubrication systems. An important factor reducing the resistance in the lubrication systems is the appearance in the region of the lubricating grease contact with the conduit wall, of the so called *the boundary layer* (or *the wall effect*) which has different rheological properties than the rest of the grease's volume. The phenomenon of the boundary layer formation while the suspension flows through the axisymmetric conduits is frequently referred to as *Segré-Silberberg's effect* or the *sigma effect*. For the first time, the phenomenon was thoroughly described in 1962 [60]. The influence of the boundary layer formation on the fall of the suspension flow resistance is particularly visible in the small diameter axisymmetric conduits where the suspension flow is laminar. It leads to the decrease in the pressure gradient along the conduit. Simultaneously with the increase in the conduit diameter, the boundary layer influence considerably decreases [61].

The first mentions of the boundary layer in the lubricating greases appeared in 1960. Bramhal and Hutton [62] carried out the research on the influence of the wall types on the boundary layer formation. The research was conducted with the use of a plunger viscometer. While doing the research, they recorded a slip in the grease, which occurred in the area of the walls. Bramhal and Hutton observed inconsiderable influence of the wall's material and the wall surface topography on the grease slip. They explained the observed effect as a consequence of repulsion of the soap particles suspended in the base oil from the walls.

An attempt of explaining the phenomenon of the boundary layer formation in the lubricating greases within the area of the lubricating grease contact with the lubrication system conduit wall and the working surface of the sliding pair was made by Czarny. In [52,63] he proves that the boundary layer formation in the lubricating greases depends mainly on the surface material which the lubricating grease reacts with. He observed the changes of the shear stress in the commercial greases in the area of the wall made, among others, of methyl polymethacrylate, polytetrafluoroethylene, polyamide, brass, bronze, duralumin and cast iron. The phenomenon of the boundary layer formation was particularly visible at the low shear rates. According to Czarny, the boundary layer formation is an outcome of the thickener's particles adsorption on the surface of the material. Thus, during the flow of the grease, a toroidal space depleted of

the thickener is created. The number of the adsorbed thickener particles depends on the kind of grease and on the collaborating materials, and is inversely proportional to the thickener percentage.

Czarny and Moes [28] proposed a dependence describing the change of the shear stress in the lubricating grease as a function of the distance from the wall:

$$\tau = \tau_0 \left\{ 1 - e^{-\left(\frac{z+d}{s}\right)} \right\}, \quad (16)$$

where: τ_0 – yield stress, z – normal wall coordinate, d – surface layer thickness, s – thickness of the boundary layer with the exponentially decreasing yield stress, down to its minimum value on the wall $\tau = \tau_w$ (Figure 8).

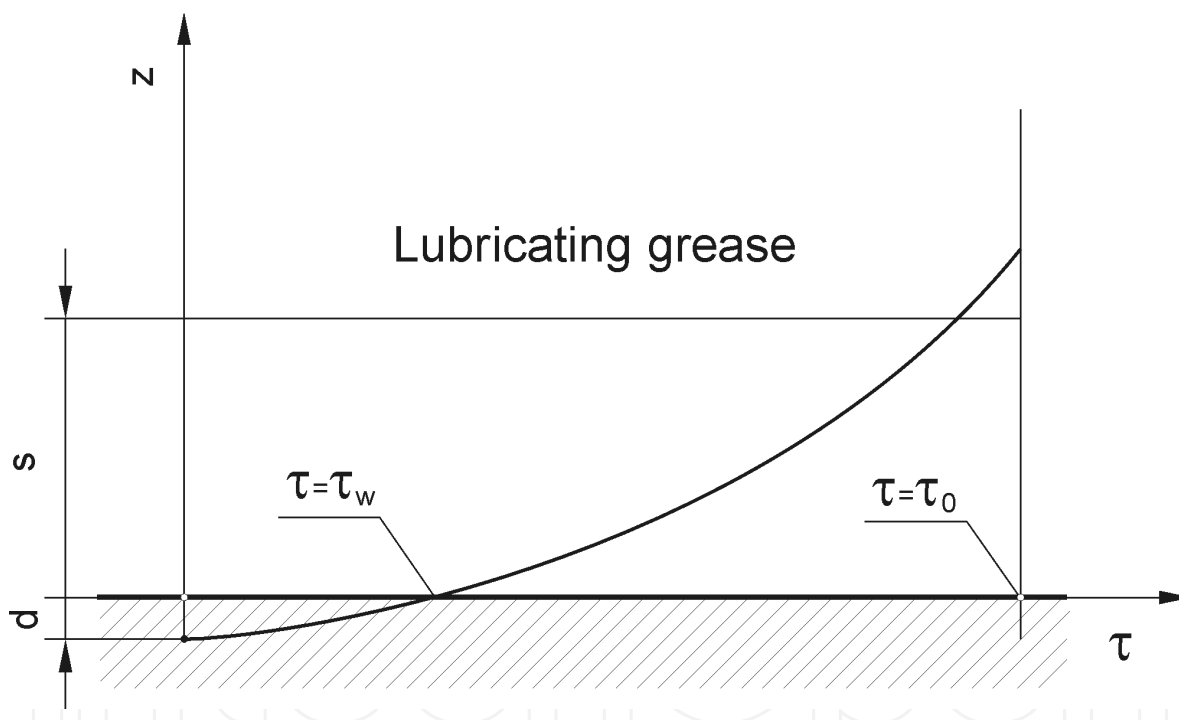


Figure 8. Stress distribution τ in the grease boundary layer as a function of the distance to wall z , according to Czarny and Moes [28].

According to Czarny, the model can be used for practical purposes at specific design solutions of lubrication systems. Parameter s and d values, needed for the determination of the stress distribution, which depend on the kind of grease, temperature of the tribological pair, the kind of the pair's wall material and its surface topography can be experimentally defined.

Czarny and Moes, during their research on the lithium soap thickened grease – Alvania EP2, found that the value of the yield stress in the grease mass τ_0 and at the wall τ_w rise along with

the increase of the grease consistency level. Simultaneously, the increase determines the reduction in the thickness of boundary layer s and surface layer d . The observed boundary layer thickness s and surface layer d equaled, in the case of Alvania EP2, respectively 3.0-9.5 and 0.6-1.5 μm . According to Czarny, the boundary layer formation in the lubricating greases is catalyzed by different thickener particles size as well as the lubricating grease temperature. Along with the temperature increase, the thickness of the absorbed layer d increases. Czarny explains the increase by an easier adsorption of the active soap particles on the material surface at a higher temperature. The thickest, 25 μm boundary layer of Alvania EP2 was observed at temperature of 373 K. It might be interesting to know that, for instance at temperature of 273 K, the boundary layer was approximately 2 μm thick.

Vinogradov et al. [64,65] investigated the shear stress decrease in the lubricating grease at the wall. The research was carried out on the lithium and calcium soap as well as ceresine thickened greases. All the researched lubricating greases formed the boundary layer. The experiments were conducted with the use of the rotational cone-and-plate rheometer and of the capillary rheometer. They found that the thickness of the boundary layer in the grease is determined by the stress which is present there. Based on the Herschel-Bulkley model, they defined dependences which enable the determination of the grease flow parameters in the gap and in the axisymmetric conduit, including the wall effect.

The research of the lubricating grease flow in the conduits was conducted also by Swartz and Hardy [66]. They recorded a decrease in resistance of the lubricating grease flow through the steel axisymmetric conduits. According to their hypothesis, it was caused by bleeding of the base oil on the conduit wall and by repulsing the thickener particles from the wall. The hypothesis, however, was not experimentally verified.

Biernacki in [67-69] investigated the problem of influence of the wall material and of the grease temperature on the boundary layer formation. He studied the phenomenon of the boundary layer formation in the commercial greases, in the area of the walls made of plastics (polyamide, polyvinyl chloride, methyl polymethacrylate, polytetrafluoroethylene) as well as the walls made of metal (steel, copper, mazak, duralumin, aluminium) of different surface topography. The research was carried out mainly with the use of the rotational coaxial cylinder rheometer. In the lithium and calcium greases he recorded lower shear stress values at the walls of the cylinders made of metal than at those made of plastics. The differences in the shear stress values were particularly visible in the low shear rates range and at the low temperature. With the increase of temperature and the shear stress, the differences in the values of the shear stress in the greases depending on the wall material disappear. In the polymer and aluminium greases Biernacki did not observe considerable differences in the shear stress values recorded at the surface of the walls made of different materials.

Biernacki also investigated the problem of the boundary layer thickness in the complex lithium and bentonite greases in the area of two copper and polypropylene plates which approach parallel to each other. The experiment showed that the lithium grease at the copper plate forms a 65 μm thick boundary layer. The depleted part of the lithium thickener was formed 27 μm from the plate surface. Biernacki did not observe the boundary layer formation in the lithium

grease at the polypropylene plate. In the bentonite grease, the boundary layer was not formed in any of the cases.

Delgado et al. in [70-72] did research on the influence of air, roughness of the steel conduit wall surface, as well as the conduit diameter on the pressure drop at the horizontal flow of the grease. They observed that the roughness of the conduit wall influences the formation of the boundary layer in the lubricating grease. The reduction of the surface roughness considerably reduced the pressure gradient. The differences grew with the conduit diameter reduction or with the grease flow rise. Delgado et al. also found out that the air present in the lubricating grease causes the reduction of the wall slip. According to their hypothesis, it is caused by the fact that the air in the lubricating grease generates considerable differences in the moistening of the internal walls of the conduit. The research was carried out mainly on the complex soap lubricants.

6. Conclusions

A conclusion of the presented research is that the flow of the plastic greases in the lubrication systems depends not only on the design of the systems but also on the kind of grease. Greases are non-Newtonian fluids of a highly complex structure, and therefore the to carry out the evaluation process of their behaviour in particular conditions is multi-stage and very difficult. The flow resistance of the grease in particular elements of the lubrication system depend, among others, on the structural viscosity of the grease. All greases get thinned, to a larger or smaller extent, in the shearing process. At the distribution of the grease to the friction nodes in a particular period of time, the flow resistance gets reduced as a result of the grease thickener's microstructure degradation. The decrease in the grease flow resistance is strictly correlated with the decrease of the shear stress in the grease. In the first seconds of supplying a new portion of the grease into the main conduit of the lubrication system, the pump must in the first place overcome the flow resistance generated by the grease, which is connected with the occurrence of the yield stress in the grease. The value of the stress, as well as the characteristics of the shear thinning for a particular grease, among other factors, depend on the flow rate generated by the lubrication pump, but also on the physical and chemical activity of the environment. An important determinant on the generating the flow resistance in the lubrication systems are the physical-chemical phenomena connected with the interaction of the grease thickener particles suspended in the base oil. One of them is a phenomenon of the grease thixotropy, consisting in its gel→sol→gel transition, namely the reduction in the grease structural viscosity at its flow and a partial thickener microstructure reconstruction in the phase of the grease relaxation, between the consecutive cycles of its distribution to the friction nodes. The phenomenon is crucial in the case of the greases which stay in the conduits and dividers of the lubrication system. It can be dangerous for the complex systems, working cyclically (for instance, the central lubrication systems of big mining machines). A short-term, uncontrolled increase in the flow resistance in such systems may lead to the excessive energy consumption by the pump, and in the extreme cases, to damage of the charging unit, and consequently, to the system failure.

Critical for the question of the flow resistance is also the material used for the making of the lubrication conduits as well as their surface topography. Some materials (copper, steel and cast iron in particular) show the increased adsorption of the particles of the thickener on their surface. It results in the generation of certain thickener depleted zones, in a shape of a ring, presenting a lower structural viscosity. The flow resistance at the start of the pump dosing the grease depending on the material of which the lubrication conduit is made, can be reduced even by half. In the case when the roughness of the internal surface finish of the conduit is higher or equal to the thickness of the thickener depleted layer, then the grease flow resistance is considerably higher than the one which would be observed at the smooth surface finish. While designing the lubrication systems, it is critical to pay attention to whether the roughness of the lubrication conduit surface are as low as possible. It is important to mention here that the pressure drops connected with the resistance, in the majority of the lubrication system elements are local in their character, whereas in the lubrication conduits, there are constant pressure drops. In the case of the particularly long conduits, the flow resistance for the entire lubrication system is predominant there. Other elements which can increase the lubricant flow resistance as well as the pressure in the system are various types of gaps in dividers. Also in this case, their shape, section area and the material of which they are made are important. Similarly complex is a problem of determining the resistance generated by the very friction nodes and defining the pressure necessary to deliver the required grease portion to the bearing. The most important design characteristics of the delivered grease flow resistance reduction bearings are primarily their shape, dimensions of the bearings' working side surfaces, the distribution and way the lubrication gaps are cut, as well as the circumferential backlash.

Nomenclature

m – index exponent

α_1 – the not entangled particles shear stress, Pa

α_2 – the entangled particles shear stress, Pa

β_1 – shear intensity for the not entangled particles, s^{-1}

β_2 – shear intensity for the entangled particles, s^{-1}

γ_C – critical strain, %

$\dot{\gamma}$ – shear rate, s^{-1}

η – apparent viscosity (dynamic viscosity), Pas

η_0 – viscosity at zero shear rate, Pas

η_∞ – viscosity at infinite shear rate, Pas

η' – viscous component, Pas

η'' – elastic component, Pas

$|\eta^*|$ – complex viscosity, Pas

θ – thixotropy coefficient

λ – time-constant, s

μ – friction coefficient

τ – shear stress, Pa

τ_0 – yield stress, Pa

χ_1 – share of the not entangled particles

χ_2 – share of the entangled particles

a – rheological parameter

d – surface layer thickness, μm

d_e – average diameter of the microcontact, mm

e_{rh} – sum of the rheological energy densities in the region of all microcontacts, J/mm^3

e_{rh_e} – rheological density of energy in the microcontact region, J/mm^3

G' – storagemodulus, Pa

G'' – lossmodulus, Pa

G_N^0 – plateau modulus, Pa

$|G^*|$ – complex modulus, Pa

h_o^* – average lubrication film thickness, mm

i_{rh} – friction intensity

k – Boltzmann constant, J/K

k_b – parameter determining the time of the not entangled \rightarrow entangled particles

k_c – consistency factor of the thickener in the grease, Pas

k_f – parameter determining the time of the entangled particles \rightarrow not entangled particles
reaction m – index exponent

n – index exponent

p_r – pressure, MPa

s – thickness of the boundary layer with the exponentially decreasing yield stress, μm

T – temperature, K

w – elastic strain energy of the entangled particles

w' – elastic strain energy of the not entangled particles

z – normal wall coordinate

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References

- [1] Czarny, R. Lubricating Greases. Warsaw: WNT Publishers, (2004) (in Polish).
- [2] Vold JM. Colloidal Structure in Lithium Stearate Greases. *Physical Chemistry* 1956;60(4) 439-442.
- [3] Farrington BB, Davis WN. Structure of Lubricating Greases. *Industrial and Engineering Chemistry* 1936;28(4) 414-416.
- [4] IshchukYuL. Lubricating Grease Manufacturing Technology. New Delhi: New Age International Limited Publishers, 2005.
- [5] Boner CJ. Modern Lubricating Greases, Broseley: Scientific Publication; 1976.
- [6] Czarny R. Effect of Changes in Grease Structure on Sliding Friction, *Industrial Lubrication and Tribology* 1995;47 3-7.
- [7] Froischteter GB, Trilisky KK, IshchukYuL, Stupak PM. Rheological and Thermophysical Properties of Greases. London: Gordon & Breach Science Publishers, 1989.
- [8] Basiński A et al. Polish Dictionary of Chemical Terminology. Warsaw: WNT Publishers; 1975 (in Polish).
- [9] Czarny R. Investigation into Phenomena Accompanying the Flow of Greases in Lubrication Systems. Wroclaw: Publishing House of the Wroclaw University of Technology; 1992 (in Polish).

- [10] Mewis J. Thixotropy – A General Review, *Journal of Non-Newtonian Fluid Mechanics* 1979;6 1-20.
- [11] Luckham PF, Rossi S. The Colloidal and Rheological Properties of Bentonite Suspensions. *Advances in Colloid and Interface Science* 1999;82 43-92.
- [12] Delgado MA, Valencia C, Sanchez MC, Franco JM, Gallegos C. Influence of Soap Concentration and Oil Viscosity on the Rheology and Microstructure of Lubricating Greases. *Industrial and Engineering Chemistry Research* 2006;45(6) 1902-1910.
- [13] Moore RJ, Cravath AM. Mechanical Breakdown of Soap-base Greases, *Industrial and Engineering Chemistry* 1951;43(12) 2892-2897.
- [14] Yeong SK, Luckham PF, TadrosThF. Steady Flow and Viscoelastic Properties of Lubricating Grease Containing Various Thickener Concentrations. *Journal of Colloid and Interface Science* 2004;274 285-293.
- [15] Cann PM. Grease Degradation in Bearing Simulation Device. *Tribology International* 2006;39 1698-1706.
- [16] Cousseau T, Graca BM, Campos AV, Seabra JHO. Influence of Grease Rheology on Thrust Ball Bearings Friction Torque, *Tribology International* 2012;46 106-113.
- [17] Farcas F, Gafitanu MD. Some Influence Parameters on Grease Lubricated Rolling Contacts Service Life. *Wear* 1999;225-229 1004-1010.
- [18] Vinogradov GV, DeinegaYuF, VerbitskyYaA. Thixotropy of Greases and Low-speed Operation of Rotational Plastoviscometers and Rolling Bearings. *RheologicaActa* 1967; 6(3) 252-259.
- [19] CannPM, Spikes HA. Film Thickness Measurements of Lubricating Grease Under Normally Starved Conditions. *NLGI Spokesman* 1992;56 (2) 21-26.
- [20] Wiliamson BP, Kendal DR, Cann PM. The Influence of Grease Composition on Film Thickness in EHD Contacts. *NLGI Spokesmen* 1993;57(8) 13-18.
- [21] Krawiec S. On the Mechanism of the Synergistic Effect of PTFE and Copper in a Lithium Grease Lubricant. *Industrial Lubrication and Tribology* 2011;63(3) 171-177.
- [22] Krawiec S. The Synergistic Effect of Copper Powder with PTFE in a Grease Lubricant Under Mixed Friction Conditions. *Archives of Civil and Mechanical Engineering* 2011;11(2) 379-390.
- [23] Czarny R, Paszkowski M. Einfluss von Zusätzen auf die rheologischen Eigenschaften der Schmierfette, 15th International Colloquium Tribology. *Automotive and Industrial Lubrication*, 2006, Stuttgart-Ostfildern, Germany.
- [24] Czarny R, Paszkowski M. The Influence of Graphite Solid Additives, MoS₂ and PTFE on Changes in Shear Stress Values in Lubricating Greases. *Journal of Synthetic Lubrication* 2007;24(1) 19-29.

- [25] Herschel WH, Bulkley R. Measurement of Consistency as Applied to Rubber – Benzene Solutions. *Proceedings of American Society of Testing Materials* 1926;26, 621-633.
- [26] Yasuda K, Armstrong R, Cohen RE. Shear Flow Properties of Concentrated Solutions of Linear and Star Branched Polystyrenes. *RheologicaActa* 1981;20 163-178.
- [27] Bird R, Armstrong R, Hassager O. *Dynamics of Polymer Liquids: Volume 1. Fluid Mechanics*. New York: John Wiley & Sons; 1987.
- [28] Czarny R, Moes H. Some Aspects of Lubricating Grease Flow, 3rd International Tribology Congress – Eurotrib '81, 1981, Warsaw, Poland.
- [29] Liu Ch, He J, Ruymbeke E, Keunings R, Bailly C. Evaluation of Different Methods for the Determination of the Plateau Modulus and the Entanglement Molecular Weight. *Polymer* 2006;47 4461–4479.
- [30] Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, Gallegos C. Recycled and Virgin LDPE as Rheology Modifiers of Lithium Lubricating Greases: A Comparative Study. *Polymer Engineering and Science* 2008;48 1112–1119.
- [31] Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, Gallegos C. Rheological Modification of Lubricating Greases with Recycled Polymers from Different Plastics Waste. *Industrial & Engineering Chemistry Research* 2009;48 4136–4144.
- [32] Péterfi T. Die Abhebung der Befruchtungsmembran bei Seeigeleiern. *Archiv für Entwicklungsmechanik der Organismen* 1927;112 660-695.
- [33] Lagaly G, Beneke K. *Eighty years of colloid science in Hungary and Germany*. University Kiel, 2002.
- [34] Freundlich H. *Thixotropie*. Paris: Hermann, 1935.
- [35] Efremov IF, Us'yarov OG. The Long-range Interaction Between Colloid and Other Particles and the Formation of Periodic Colloid Structures. *Russian Chemical Reviews* 1976;45(5) 435-453.
- [36] Efremov IF. The Dilatancy of Colloidal Structures and Polymer Solutions, *Russian Chemical Reviews* 1982;51(2) 160-177.
- [37] Sonntag H. *Lehrbuch der Kolloidwissenschaft*. Berlin: VEB Deutscher Verlag der Wissenschaften, 1977.
- [38] Scheludko A. *Colloid Chemistry*. Warsaw: WNT Publishers, 1969. Translated from Russian by Siedlecka Z (in Polish).
- [39] Barnes HA. Thixotropy – a Review. *Journal of Non-Newtonian Fluid Mechanics* 1997;70 1-33.

- [40] Franco JM, Delgado MA, Valencia C. Combined Oxidative-shear Resistance of Castrol Oil-based Lubricating Greases, 3rd Arnold Tross Colloquium, 2007, Hamburg, Germany.
- [41] Renshaw TA. Effect of Shear on Lithium Greases and Their Soap Phase. *Industrial and Engineering Chemistry* 1955;47(4) 834-838.
- [42] Sirianni AF, Moses GB, Puddington IE. Particle Shape in Thixotropic Suspensions. *Canadian Journal of Chemistry* 1951;29 166-172.
- [43] Goodeve CF, Whitfield GW, The Measurement of Thixotropy in Absolute Units. *Transaction of Faraday Society* 1938;34 511-520.
- [44] [44] Arnold JE, Goodeve CF. The Coefficient of Thixotropy of Suspensions of Carbon Black in Mineral Oil. *Journal of Physical Chemistry* 1940;44(5) 652-670.
- [45] Moses GB, Puddington IE. Rheological Properties of Some Soap-Oil Systems, *Canadian Journal of Chemistry* 1951;29 996-1009.
- [46] Hahn SJ, Ree T, Eyring H. A Theory of Thixotropy and its Application to Grease. *NLGI Spokesman* 1957;21(3) 12-20.
- [47] Houser EA, Reed CE. Studies in Thixotropy II – The Thixotropic Behavior and Structure of Bentonite. *Journal of Physical Chemistry* 1937;41(7) 911-934.
- [48] Hahn SJ, Eyring H, Higuchi I, Ree T. Flow Properties of Lubricating Oils Under Pressure. *NLGI Spokesman* 1958;21(3) 123-128.
- [49] Utsugi H, Kim K, Ree T, Eyring H. Thixotropy Property of Lubricating Grease, *NLGI Spokesman*, NLGI 28th Annual Meeting, 1960, Chicago, USA.
- [50] Bair S. Actual Eyring Models for Thixotropy and Shear-thinning: Experimental Validation and Application to EHD. *ASME Journal of Tribology* 2004;126 728-732.
- [51] Sacchetti M, Magnin A, Piau JM, Pierrard JM. Caractérisation d'une graisse lubrifiante en écoulements viscosimétriques transitoires. *Journal of Theoretical and Applied Mechanics, Numérospecial* 1985; 165-199.
- [52] Czarny R. Influence of the Lubricating Grease Structure on its Rheological Properties. *Scientific Works of the Institute of Machine Design and Operation of Wroclaw University of Technology. Problems of Friction, Lubrication and Machine System Computerization*. Wroclaw: Publishing House of Wroclaw University of Technology; 1989 (in Polish).
- [53] Czarny R. Effect of Temperature on the Thixotropy Phenomenon in Lubricating Greases, *Proceedings of the Japan International Tribology Conference*, 1990, Nagoya, Japan.
- [54] Kuhn E. An Energy Interpretation of Thixotropic Effect. *Wear* 1991;142(1991) 203-205.

- [55] Czarny R. Einfluss der Thixotropie auf die rheologischen Eigenschaften der Schmierfette. *Tribologie und Schmierungstechnik* 1989;3 (36) 134-140.
- [56] Kuhn E. Energy Investigation of the Rheological Wear of Lubricant Greases. *Applied Rheology* 1992;2(4) 252-257.
- [57] Kuhn E. Description of the Energy Level of Tribologically Stressed Greases. *Wear* 1995;188(1995) 138-141.
- [58] Kuhn E, Balan C. Experimental Procedure for the Evaluation of the Friction Energy of Lubricating Greases. *Wear* 1997;209(1997) 237-240.
- [59] Kuhn E. Experimental Grease Investigation From an Energy Point of View. *Industrial Lubricating and Tribology* 1999;51(5) 246-251.
- [60] Segré G, Silberberg A. Behavior of Macroscopic Rigid Spheres in Poiseuille Flow. Part II. Experimental Results and Interpretation. *Journal of fluid mechanics* 1962;14 136-157.
- [61] Heywood NI, Cheng DC-H. Flow in Pipes. Part II. Multiphase flow. *Physics in Technology* 1984;15.
- [62] Bramhall AD, Hutton JF. Wall Effect in the Flow of Lubricating Greases in Plunger Viscometers. *British Journal of Applied Physics* 1960;11 363-369.
- [63] Czarny R. Influence of the Wall Type on Formation of the Grease Wall Effect, Conference materials, XXI Autumn Tribological School – Machine and appliance friction pairs lubrication. Contemporary tendencies in the research theory development, 1996, Lodz – Arturowek, Poland (in Polish).
- [64] Vinogradov GV, Froishteter GB, Trilsky KK. The Generalized Theory of Flow of Plastic Disperse Systems with Account of the Wall Effect. *RheologicaActa* 1978;17(2) 156-165.
- [65] Vinogradov GV, Froishteter GB, Trilsky KK, Smorodinsky EL. The Flow of Plastic Disperse Systems in the Presence of the Wall Effect. *RheologicaActa* 1975;14(9) 765-775.
- [66] Swartz CJ, Hardy B. Mathematical Model of Grease Flow in Pipes. *NLGI Spokesman* 1991;55(3) 14 –17.
- [67] Biernacki K. Influence of Surface Roughness and Temperature on the Lubricating Grease Flow in the Boundary Layer. *Tribologia* 2000;2 187-198 (in Polish).
- [68] Biernacki K, Czarny R. Influence of the Wall Material and Temperature on the Rheological Properties of the Boundary Layer in the Lithium and Calcium Greases. *Hydraulika i Pneumatyka* 2002;4 24-25 (in Polish).
- [69] Biernacki K. Analysis of the Wall Effect in Lubricating Greases. *Tribologia* 2006;5 111-129 (in Polish).

- [70] Delgado MA, Franco JM, Partal P, Gallegos C. Experimental Study of Grease Flow in Pipelines: Wall Slip and Air Entrainment Effects. *Chemical Engineering and Processing* 2005;44 805–817.
- [71] Ruiz-Viera MJ, Delgado MA, Franco JM, Gallegos C. Evaluation of Wall Slip Effects in the Lubricating Grease/Air Two-phase Flow Along Pipelines. *Journal of Non-Newtonian Fluid Mechanics* 2005;139 190–196.
- [72] Ruiz-Viera MJ, Delgado MA, Franco JM, Sanchez MC, Gallegos C. On the Drag Reduction for the Two-phase Horizontal Pipe Flow of Highly Viscous Non-Newtonian Liquid/Air Mixtures: Case of Lubricating Grease. *International Journal of Multiphase Flow* 2006;32 232–247.

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