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The influence of type of dispersed phase on rolling contact fatigue of lubricating greases on mineral base oil

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ABSTRACT

The paper discusses the influence of type dispersed phase on value of rolling contact fatigue of bearings lubricated with selected lubricating compositions. The compositions, which were produced on the mineral base oil were thickened of lithium stearate, calcium stearate, aluminum stearate, lithium complex soap and modified silica, montmorillonite, and polytetrafluoroethylene were evaluated.

Were carried out the investigations of rolling contact fatigue (pitting) of bearings, which were lubricated of the compositions prepared on the above-mentioned thickeners. Then was evaluated the influence of various thickeners on changes of rolling contact fatigue. The tribological tests were carried out using T-03 four-ball machine under high load conditions.

On the basis of obtained results it may be concluded, that used of thickeners such as: modified amorphous silica, montmorillonite and polytetrafluoroethylene to produce of lubricating compositions, positively affected on the change of rolling contact fatigue of tribosystems lubricated with the above-mentioned compositions in comparison to the compositions, when as a dispersed phase were used a soap thickeners.

Keywords: dispersed phase, thickener, lubricating grease, rolling contact fatigue, pitting, Weibull curve.

1. Introduction

One of the components of lubricating grease is a thickener. It is a substance, which was provided a spatial structural arrangement and suitable rheological and tribological properties of prepared lubricating grease. The content of thickener in the lubricating grease was from 5% to 30% and depends on the type of thickener and consistency of lubricating grease [1]. From the type of thickener will depend a series of operational characteristics of lubricating greases such as: texture, mechanical stability, temperature stability, rheological properties or resistance on action of water and acids [2].

One of the generally used classifications of lubricating greases is a classification based on the type of the thickener. On this basis were stand out the greases: soap (e.g.: on the lithium stearate), mixed (e.g.: on the lithium-calcium soaps), inorganic (e.g.: on the silica or bentonite) and polymeric (e.g.: on the polyurethane or terephthalates) [3].

Nowadays increasingly meaning at production of lubricating greases has a complex and organic thickeners. The complex compounds, which were used as a thickeners of lubricating greases were increased the dropping point of the produced lubricating composition, thereupon was raised the maximum temperature of the applicability of such product. The incorporation of these types of thickeners in the structure of lubricating greases was increased of the resistance on action of water, improved the mechanical and structural stability and lubricating properties (especially antiseizure). Therefore increasingly the complex thickeners were displaced from field of conventional thickeners such as e.g. the simple soaps [4].

However the organic thickeners such as a metal salts of I and II groups of the periodic table and highlymolecular fatty acids are strong oxidizers and has a high thermal stability, and the lubricating greases thickened with these substances has a high of durability of exploitation [5]. An important meaning has inorganic thickeners, which may include the colloidal silica and montmorillonite. They improved the chemical stability and lubricating properties of produced lubricating compositions, thereupon on the worlds fields were followed an increase of interest in this type of thickeners [6-12].

The one of the most frequent forms of wear, which deteriorates the working elements of machines and devices is surface fatigue wear, so-called pitting. This type of wear is caused by the cyclic stresses in the areas where the material is in contact with the lubricant. The cause of pitting is the fatigue of the surface layer. The process of spall wear consists of three phases: the early formation of cracks due to fatigue, the extension of the cracks due injection of the lubricating grease, and finally pulling out the particles of material from the surface layer. The surface fatigue wear depends on many factors, e.g. the properties of the material, the conditions of working, the construction of the tribosystem or physicochemical properties of the lubricating compositions [13-19]. This form of wear is characteristic for rolling friction with the sidle, as well as for dry friction and leads to the loss of properties of the lubricated elements.

The aim of this work was the analysis of influence of the type of the dispersed phase used to prepare of lubricating compositions on the rolling contact fatigue of bearings in food industry developed at the Research Network LUKASIEWICZ - Institute for Sustainable Technologies in Radom.

2. The subject and methodology of research

A group of model lubricating compositions made of non-toxic components were prepared to determine of dispersion and dispersed phase. As a dispersion phase was used a paraffin oil about the pharmaceutical grade [20]. However as a solid phase (dispersed) were used: the lithium stearate [21-24], the calcium stearate [25], the aluminum stearate [23-24,26], the 12-hydroxystearate-adipate (1:0,25) of lithium [27], the amorphous silica Aerosil has a particle size of 7 – 40 nm [28], montmorillonite [29] and polytetrafluoroethylene [30].

Each of the above-mentioned thickeners was introduced to the base oil in an amount of 12% m/m. So formed lubricating compositions was determined of symbols A, B, C, D, E, F and G. In the early phase of the experiment was taken the research to the above an amount of the thickener to be introduces into to the lubricating composition. The tests were carried out with the compositions containing from 5% to 30% of thickener. The so-prepared lubricating compositions were tested on their tribological properties.

The tribological properties of the lubricating compositions were evaluated according to a standardized procedure described in IP 300/82 on a modified four-ball machine T-03. The evaluation procedure was based on the estimation of surface fatigue wear of the rolling tribosystem during 24 runs under constant load of 5886 N and constant speed of 1450 rpm. The actual test elements were the ½″ bearing balls made of 100Cr6 steel, which surface roughness was 0,032 mm and hardness was about 60-65 HRC. The test set-up was constantly measured for vibrations and the test was automatically intermitted when the permissible level of vibrations reached the defined limit. The run was accepted, when crumbling appeared on the top ball. If chipping occurred on one of the lower balls, the run was rejected. The result of each run is defined by the time in minutes. The results of individual runs were ranked from the shortest to the longest. Each result received the percentage value of probability of the ball damage. According to the IP 300/82 [31] standard method, the time vs. probability of damage were marked on the Weibull graph. Such prepared graphs provided the values of L10 and L50, defining the durability of the tribosystem at 10% and 50% probability of damage, respectively [32-35]. On the basis of pitting time values, the accumulated percentage of damages was calculated as follows:

Table 1. The chemical composition of lubricating greases

Marking of the tested grease	Dispersion phase	Dispersed phase
A	Paraffin oil	Lithium stearate
B	Paraffin oil	Calcium stearate
C	Paraffin oil	Aluminum stearate
D	Paraffin oil	12-hydroxystearate-adipate (1:0,25) of lithium
E	Paraffin oil	Modified Aerosil
F	Paraffin oil	Montmorillonite
G	Paraffin oil	Polytetrafluoro-ethylene

the probability of damage = $i/(n+1)*100\%$

where:

i – the run number,
n – the number of runs terminated with pitting ($n=24$).

The XPS analysis was carried out using a spectrometer by PREVAC. In order to remove from the surface of the specimen the adsorbed foreign substances and products the oxidation, initial surface cleaning of the specimen was conducted using the ion mill Ar+. To induce excitation in the specimen, an X-ray lamp equipped with the standard achromatic source of X-rays, accompanied by a double anode Al/Mg, were used. The main ion sputtering (for creating depth profiles) was conducted with 5 kV beam, with a current of 10 mA, and current density at 147 μA/cm^2. Survey analyses after each cycle of ion sputtering were conducted using radiation Al Kα energy 1486.6 eV, with a transition energy of 200 eV and an increment of 200 meV. The parameters for creating a detailed spectrum for each element were selected individually, taking into account the power of the X-ray excitation, the element, sampling density, transition energy, and slits of the analyser lenses. These parameters were set in such a way so that the quality of the obtained spectra was the highest. The recorded spectra were subjected to a detailed digital analysis, based on which the quantitative composition of elements in subsequent layers was established [36,37].

A confocal dispersive Raman NRS 5100 microspectometer (Jasco Corporation, Japan) equipped with an excitation laser with a wavelength of 532.12 nm and a CCD detector was used to test the chemical composition of lubricating greases after tribological tests. The parameters of the spectrometer were as follows: diffraction grating 2400 lines/mm, laser power 3.6 mW, numerical aperture 3000 μm, spectral range 3700÷200 cm^{-1}, resolution 2.1 cm^{-1}, magnification of the lens 20x, exposure time 40 s. The test material were steel balls after tribological tests [38].

3. Results and discussion

On Fig.1-7 presents theWeibull graphs obtained for the lubricating compositions based on mineral base oil and thickened of the lithium stearate, calcium stearate, aluminum stearate, 12-hydroxystearate-adipate (1:0,25) of lithium, amorphous silica Aerosil about the size particles of 7-40 nm, montmorillonite and polytetrafluoroethylene. The formulas and the R^2 correlation coefficients are included.

On the basis of obtained results the author calculated the time, after which 10% and 50% of the tested tribosystems were damaged – L10 and L50, respectively. These results are shown in Fig. 8-9.

Analyzing the presented above graphs it should be ascertained, that the rolling contact fatigue of tribosystem lubricated of tested lubricating compositions were submitted a essential changes in depending on the use of thickener. At the probability occurrence of damage, which was 10% (L10) the time of occurrence of pitting for the lubricating compositions, in which the dispersed phase were a soap thickeners was accordingly: 47.52 min for the composition thickened of lithium stearate, 43.21 min for grease thickened of calcium stearate and 38.73 min for a composition, wherein the dispersed phase was aluminum stearate. Thus, there weren't observe a significant differences of durability fatigue for the composition, in which were used a soap thickeners. A higher value of this parameter was observed for composition, which was thickened of 12-hydroxystearate-adipate (1:0,25) of lithium. In this case, coefficient L10 was 70.44 min. However, in lubricating compositions, in which a dispersed phase were used a amorphous silica Aerosil, montmorillonite and polytetrafluoroethylene the coefficient L10 was accordingly: 110.58 min; 94.88 min and 104.71 min. It was observed more than a twice increase of durability of tribosystem at 10% probability occurrence of damage for the composition, in which were used the thickeners such as: amorphous silica, montmorillonite, polytetrafluoroethylene in compared to compositions, in which as a dispersed phase were used a soap thickeners.

It has been reported, that an increase of durability of tribosystem at 10% the probability of occurrence of damage after using a complex lithium soap (about 48.2%), amorphous silica (about 132.7%), montmorillonite (about 99.7%) and polytetrafluoroethylene (about 120.3%) as a dispersed phase of tested lubricating greases in comparison to the composition, wherein the thickener was lithium soap.

The application of the above-mentioned thickeners as a dispersed phase of lubricating greases used in the experi-

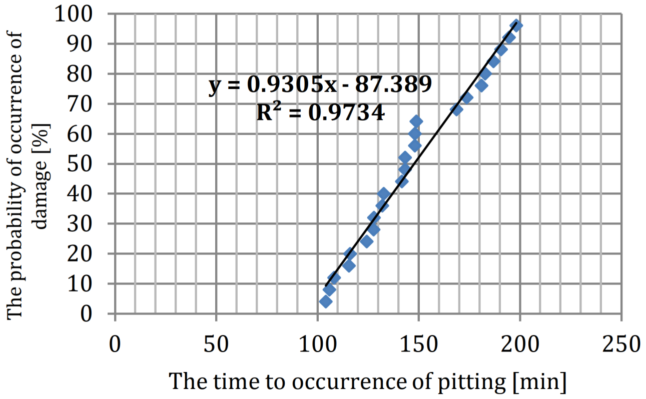

Fig.1. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of lithium stearate from time of pitting

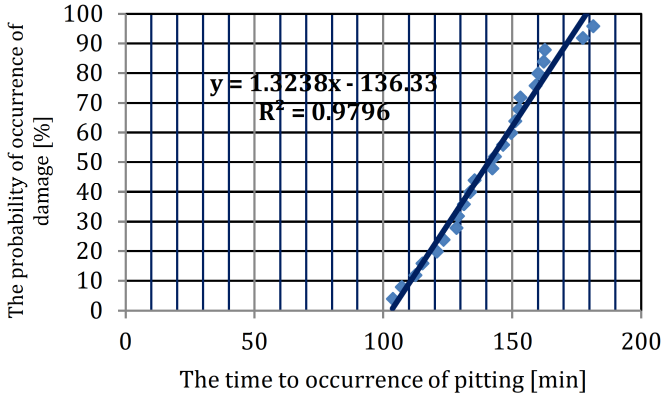

Fig.2. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of calcium stearate from time of pitting

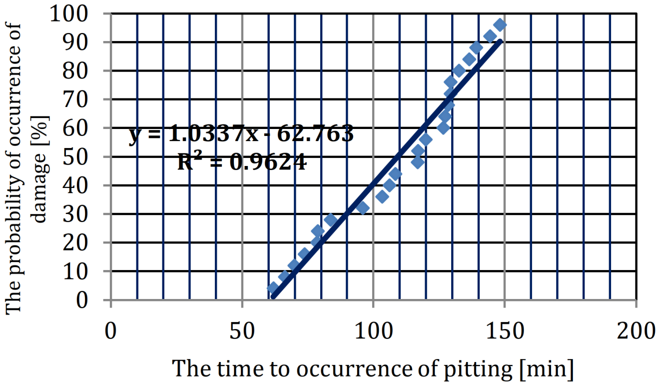

Fig.3. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of aluminum stearate from time of pitting

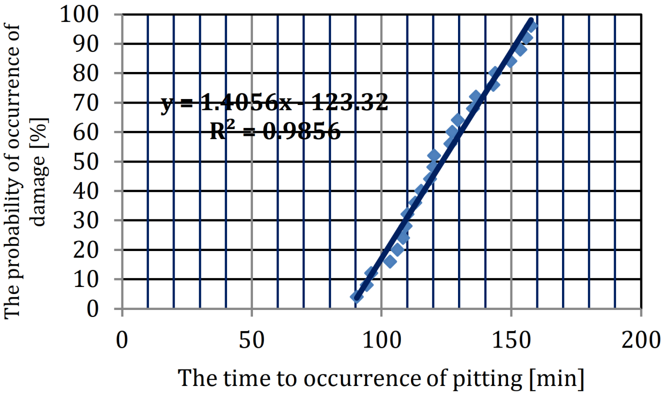

Fig.4. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of lithium 12-hydroxystearate-adipate (1:0,25) from time of pitting

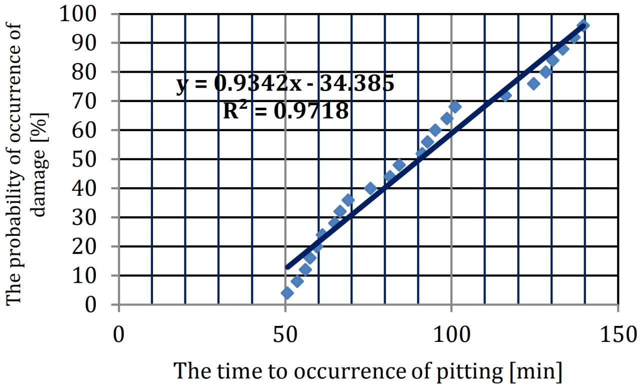

Fig.5. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of amorphous silica Aerosil from time of pitting

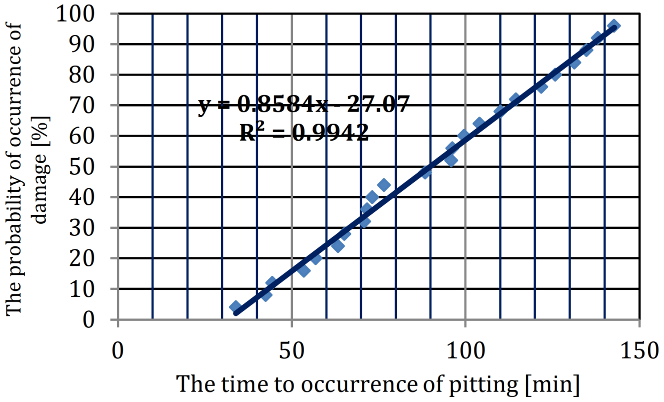

Fig.6. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of montmorillonite from time of pitting

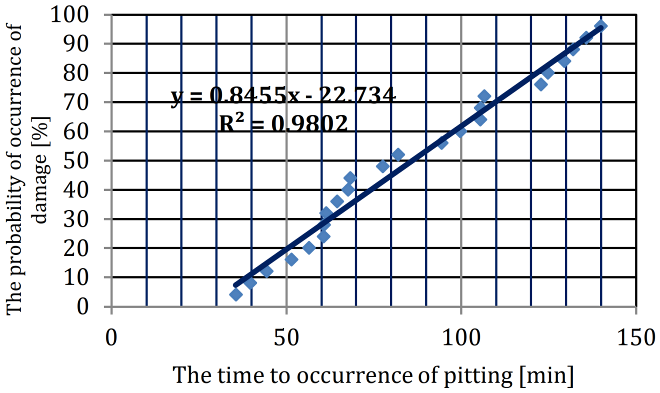

Fig.7. Dependence probability of failure of the upper ball for tribosystem lubricated grease thickened of polytetrafluoroethylene from time of pitting

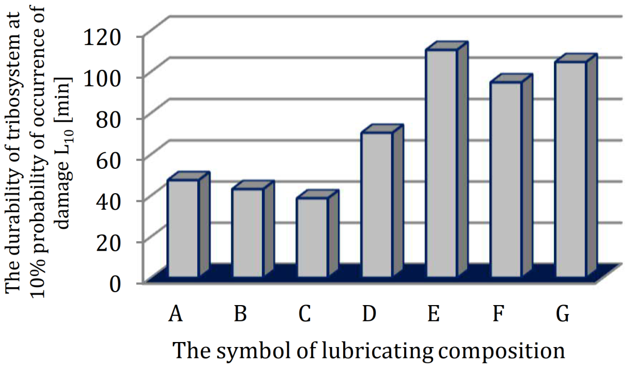

Fig.8. The comparison of fatigue live bearing – L10 - probability of failure of bearing for researches lubricating greases

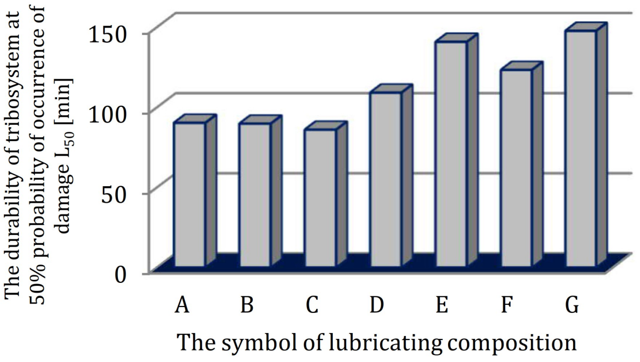

Fig.9. The comparison of fatigue live bearing – L50 - probability of failure of bearing for researches lubricating greases

ment was induced an increase of durability of tribosystem respectively: 63.0%; 155.9%; 119.6% and 142.3% in relative to the lubricating composition, wherein as a dispersed phase was used a calcium stearate.

It has been observed, that the use of a complex lithium soap, modified silica, montmorillonite and polytetrafluoroethylene as a dispersed phase of tested lubricating greases were caused an increase the durability fatigue of tribosystem at 10% the probability of occurrence of damage, respectively: 81.9%; 185.5%; 145.0% and 170.4% in compared to the lubricating composition, wherein the dispersed phase was aluminum stearate.

Thus, the used of complex lithium soap, modified silica, montmorillonite, and polytetrafluoroethylene as a dispersed phase of lubricating greases an increasing the durability of tribosystem in compared to the compositions prepared on the soap thickeners.

However at 50% the probability of occurrence of damage (L50) the time, after which it come to the pitting was: 90.34 min for composition thickened of lithium stearate, 89.83 min for grease thickened of calcium stearate and 86.07 min for composition prepared on aluminum stearate. The level of durability fatigue, which was expressed a coefficient L50 for compositions, which has been produced with the participation of soap thickeners were similar. The difference between the value of the parameter L50 for lithium and aluminum grease was only 4%. The analysis of graphs were showed, that the rolling contact fatigue of tribosystem lubricated the composition, in which as a thickener was used a 12-hydroxystearate-adipate (1:0,25) of lithium at the probability of occurrence of damage was

50% was 109.16 min. In the case of lubricating compositions thickened of amorphous silica, montmorillonite, polytetrafluoroethylene the coefficient L50 was respectively: 140.82 min; 123.35 min and 147.72 min. It has been observed an increase of durability of fatigue at 50% the probability of occurrence of damage respectively about 56%, 37% and 64% in compared to the lubricating composition, wherein as a thickener was used a lithium stearate.

The data, which were presented in the graphs indicated, that the use of complex lithium soap, modified silica, montmorillonite and polytetrafluoroethylene as a dispersed phase of tested lubricating greases were caused an increase of rolling contact fatigue life of tribosystem at 50% the probability of occurrence of damage respectively about: 21.5%; 56.8%; 37.3% and 64.4% in compared to the composition, where the dispersed phase was calcium stearate. It has been observed also an increase of rolling contact fatigue at 50% the probability of occurrence of damage about 26.9%, when was used a lithium complex soap as a thickener of tested lubricating composition, in the case of amorphous silica was noted an increase about 63.6%, in the situation of using of montmorillonite as a dispersed phase to produce of lubricating grease an increase was 43.3%, and in the case of using of polytetrafluoroethylene an increase of durability fatigue was 71.6% in compared to the lubricating composition, where as a thickener was used the aluminum stearate.

On the basis of obtained results it may be concluded, that the thickeners, which were used to produce of lubricating compositions participating in the experiment were affected variously on changes of durability fatigue of greases were produced on the basis of mineral oil. The change of durability fatigue of tested lubricating greases were depends on the type and chemical structure of used dispersed phase. The coefficients L10 and L50 were characterized the level of durability of tribosystem were indicating, that the lubricating compositions, which were prepared on mineral base oil, in which the dispersed phase were soap thickeners were shown the lower level of rolling contact fatigue than the lubricating compositions, which were thickened of amorphous silica, montmorillonite and polytetrafluoroethylene. It was observed, that the change of durability fatigue wasn't regular in all cases. The change size of rolling contact fatigue of tested lubricating compositions were depends from the chemical structure of used dispersed phase and the interaction between the dispersion and dispersed phase, which were connected to create a lubricating composition.

The various chemical structure of used thickeners was allowed ascertain, that for the tested lubricating compositions the protection against pitting was derivative of parameters which characterized the physicochemical properties of dispersed phase. The differentiation of physicochemical properties of dispersed phase was result with its different chemical structure. On the basis of this assumption it may accept the existence of the dependence between intermolecular interaction of dispersion phase (base oil) with the dispersed phase, and the tribological effectiveness of lubricating compositions, including the protection against rolling contact fatigue so called pitting.

The used of amorphous silica and montmorillonite as a thickeners of lubricating greases were an innovative method to improve of tribological characteristics. The silica is a substance with a high melting point and the boiling point and is extremely chemically resistant, moreover is nontoxic, which is extremely important at composing of biodegradable lubricants. It was used as an excellent thickener, thixotrope and anti-settling medium. The through of its polar character was easily connected with the oil molecules by van der Waals forces. The developed surface of the particles of amorphous silica was provided a high absorbability of phase oil, which was favour the efficiency of thickened and effectively modifying of the tribological properties.

The montmorillonite modified by means of quaternary ammonium salts becomes hydrophobic and organophilic, thus provided the efficient incorporation of particles the thickener in the structure of lubricating grease, even at the smooth mixing conditions. The modified was compatible in relative to the lubricating greases and used as a thickener, which effectively modifying theirs tribological properties, mainly by creating on the surface steel of low friction surface layer resistant on high load, as resulting an increased of durability fatigue.

As a dispersed phase used an electrically neutral of PTFE, which was a capability of creating on the cooperating surfaces of coating of high durability and good adsorbed on the metal surfaces. The friction was occurred in connection of metal-teflon-metal. This combination was protected lubrication of coating of teflon of microareas with cooperating surfaces without the coatings of lubricating film.

The high effectiveness action of polytetrafluoroethylene was resulted of the low temperature its decomposition, and the easier decomposition this the greater improving of durability fatigue. The thickened of the mineral oil of polytetrafluoroethylene whether amorphous silica or montmorillonite of tested lubricating compositions were caused a substantial plastification of surface, which was associated with a large reduction of stress consequential from the affects of surface roughness and was caused a increase of the durability fatigue. The use of such type thickeners was provided the creation of the limiting layers, which were efficient to regeneration, and the high degree of protection against the wear.

The reduction of durability fatigue for the composition, which was prepared on soap thickeners in comparison to other compositions used in the experiment might be caused by products of tribochemical reactions between the lubricating composition and the surface of tribosystem.

The results of testing the friction surfaces covered with mineral lubricating grease with various thickeners by means of X-ray photoelectron spectroscopy (XPS), connec-

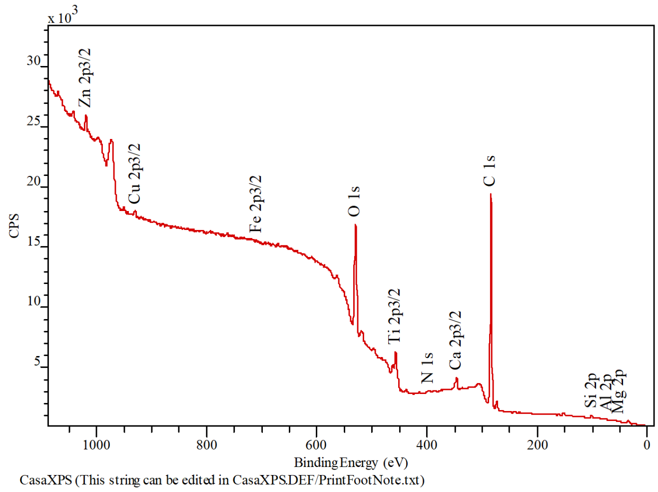

Fig.10. The XPS spectrum of steel ball before tribological

ted with ion sputtering into the surface layer, are presented in Table 2, and the example of the spectrum recording from XPS - in Fig.10. In the Fig.10 shows the relative content of the basic elements contained in the bearing steel, obtained as a result of ion sputtering and quantitative XPS analysis of the initial surface of the steel ball (before the tribological tests). As a result of the analysis, the atomic percentage of individual elements in the surface layer of steel were determined. Most likely, some of these elements were pollution from the ball production process (no presence of phosphorus was detected). In the surface layer (before the ionic sputtering), the carbon (66.70%) and oxygen (22.80%) dominated quantitatively, while the iron and copper constituted for just over 4%. After sputtering, there were found no other elements than the bearing steel components, among which the iron and copper had the largest atomic participation. The sputtering of analysed surface was effectuated with argon ions with 2 keV energy. Then sputtering of the tested area was continued with higher energy ions (4 keV). At this time, the composition of the analysed surface layer did not change significantly.

It was found, that even though, that the ball was not subjected of tribological tests and was cleaning before analysis in n-hexane, its surface layer was modified by oxygen and carbon. Probably at the stage of production of the balls and during their contact with the atmosphere, the surface layer of the steel reacted with the components of the environment with which it was in contact. In order to obtain of information about the chemical environment of the elements have a present in the surface layer of steel, a detailed analysis of XPS spectra was carried out. Probable chemical structures were determined on the basis of registered bond energies (Table 2). In Table 2 presents the results of the analysis of the state of the steel ball surface after tribological tests for mineral greases with different of thickeners. During the sputtering, a 285eV band of carbon (C1s) was observed. This energy is characteristic for the C-O bond in organic compounds, especially for carbides occurring in bearing steel. The "clean" surface layer of bearing steel is very reactive and reacts with compounds situated in its environment, hence the presence of organic compounds. In the range of oxygen photoelectrons (O1s) in the XPS spectrum, a 530 eV band (characteristic of oxygen in oxides) can be extract. The oxygen intensity of the signal is gradually decreases (along with the depth of ion sputtering), but its presence in the deeper layers proves about the penetration of the surface layer and the creating of the iron and copper oxides. Probably the oxide layer was created in the production process of the balls.

On the band with 710 eV binding energy, occurring in the spectrum of iron (Fe2p) photoelectrons, may consist of signals characteristic for carbides and oxides. A similar studies has been the trace of wear, which created under friction conditions on the ball lubricated with mineral grease with lithium soap thickener. From the analysis of the spectrum of Grease A shows, that the carbon, as with of steel surfaces before friction (Fig.10), was in a large amount in the surface layer. The oxygen was occurred also in substantial quantity. In order to examine the composition of the deeper layers, further sputtering was continued with argon ions of 4 keV energy. The oxygen content after 40 min of ion sputtering was comparable to the oxygen content in the initial steel ball after 5 min of sputtering. The studies carried out provide, that the surface layer was modified by this element during the friction process. The spectra of carbon photoelectrons, recorded on the surface of the initial ball and the ball subjected of tribological tests, were similar course, although in the case of initial surface steel the organic compounds having contamination character, and in the case of steel after friction tests, these compounds came from the lubricant (the compounds deposited in the surface layer the balls in the contact zone were removed by counter-specimen). The XPS spectra of zinc (Zn2p) photoelectrons (greases B,C, E, F and G) had a characteristic signal of zinc sulphides (1045.5 eV). This band disappeared with the depth of sputtering. The analysis of F1s photoelectrons showed that, the fluorine was present in the tested layer in the form of lithium, calcium and aluminium fluorides (grease G). Provides the signal binding energy of 689,9 eV. The intensity of this band gradually decreased with the depth of sputtering until it completely disappeared. In the range of oxygen photoelectrons in the XPS spectrum, there was a band signal with a binding energy of 530.3 eV, which was characteristic for oxygen present in oxides (greases A,B,C,D,E,F,G).This band was more intense than similar ones recorded on the initial steel surface and did not disappear after several sputtering cycles. The presence of this band provides about the modification of the surface layer by oxygen compounds. In the case of molybdenum, in the recorded XPS spectra of Mo3d photoelectrons there was a band with 235 eV energy, which quickly disappeared (characteristic for molybdenum in sulphates).

The carried out analyses showed, that the dominant form in which molybdenum was present in the analysed sample were sulphates, present in surface layers (greases A,B,C,D,E,F and G). A similar band analysis was also carried out for antimony. In the spectra of photoelectrons of

Table 2. The results of analysis of steel ball surface after tribological tests for tested lubricating compositions

The elements present in surface layer of analysed samples	The surface condition of steel ball before tribological tests	The surface condition of steel balls of tested lubricating greases after tribological tests						
		Grease A	Grease B	Grease C	Grease D	Grease E	Grease F	Grease G
		The bindingenergy/description						
Carbon – C1s	285 eV - carbides	285 eV – lithiumcarbides	285 eV – calciumcarbides	285 eV – aluminium carbides	285 eV – lithiumcarbides	285 eV – siliconcarbides	285 eV – aluminium carbides	285 eV – fluorinecarbides
Iron – Fe2p	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides	710 eV – carbides and iron oxides
Oxygen – O1s	530 eV – iron and copper oxides	530 eV – iron, copper and lithium oxides	530 eV – iron, copper and calcium oxides	530 eV – iron, copper and aluminium oxides	530 eV – iron, copper and lithium oxides	530 eV – iron and copper oxides	530 eV – iron, copper and aluminium oxides	530 eV – iron and copper oxides
Zinc – Zn2p	1045,5 eV – zincsulphides	-	1045,5 eV – zincsulphides	1045,5 eV – zincsulphides	-	1045,5 eV – zincsulphides	1045,5 eV – zincsulphides	1045,5 eV – zincsulphides
Fluorine – F1s	-	-	-	-	-	-	-	689,9 eV – lithium, aluminium and calcium fluo-
Molybdenum – Mo3d	235 eV – molybdenum sulphates	235 eV – molybdenum sulphates	235 eV – molybdenum sulphates	235 eV - molybdenum sulphates	235 eV – molybdenum sulphates	235 eV – molybdenum sulphates	235 eV – molybdenum sulphates	235 eV – molybdenum sulphates
Antimony – Sb3d	525 eV – antimonysulphates	525 eV – antimonysulphates	-	-	-	-	-	-
Nitrogen – N1s	397 eV – nitrogenoxides	397 eV – nitrogenoxides	-	397 eV – nitrogenoxides	397 eV – nitrogenoxides	397 eV – nitrogenoxides	397 eV – nitrogenoxides	397 eV – nitrogenoxides
Calcium – Ca2p	350 eV - calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates	350 eV – calcium oxides, sulphates and phosphates
Silicon – Si2p	-	-	-	-	-	102,7 eV – silicon oxides and sulphates	103,5 eV – aluminosilicates, silicon sulphates and	-
Lithium – Li1s	-	55,6 eV – lithiumsulphates, phosphates	-	-	55,6 eV - lithiumsulphates, phosphates	-	-	-
Sodium – Na1s	-	-	-	-	-	-	-	1071,3 eV – sodium sulphates and
Magnesium – Mg1s	-	-	1304,7 eV – magnesium oxides and sulphates	-	-	-	-	1305,8 eV – magnesium sulphates, phosphates
Aluminium – Al2p	-	-	-	74,6 eV – aluminium oxides, phosphates and sulphates	-	-	74,6 eV - aluminium oxides and aluminosilicates	74,4 eV - aluminium oxides, phosphates and fluorides

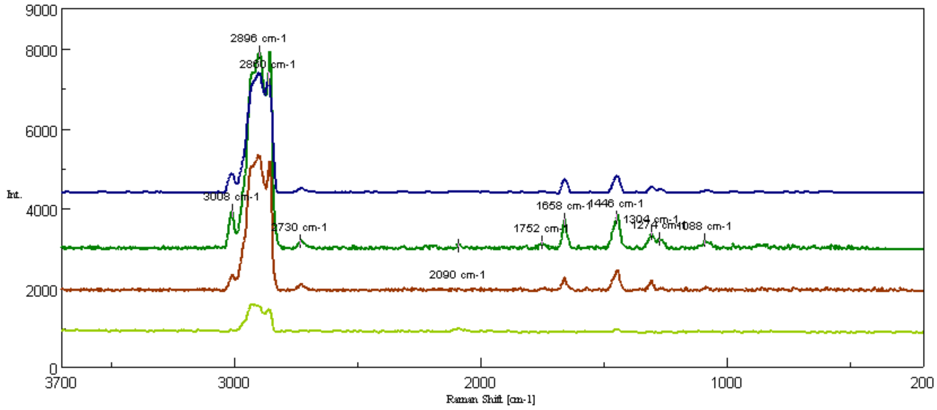

Fig.11. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 3700 cm^{-1} – 200 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of calcium stearate (brown), thickened of aluminium stearate (dark green) and thickened of lithium 12-hydroxystearate-adipate (blue)

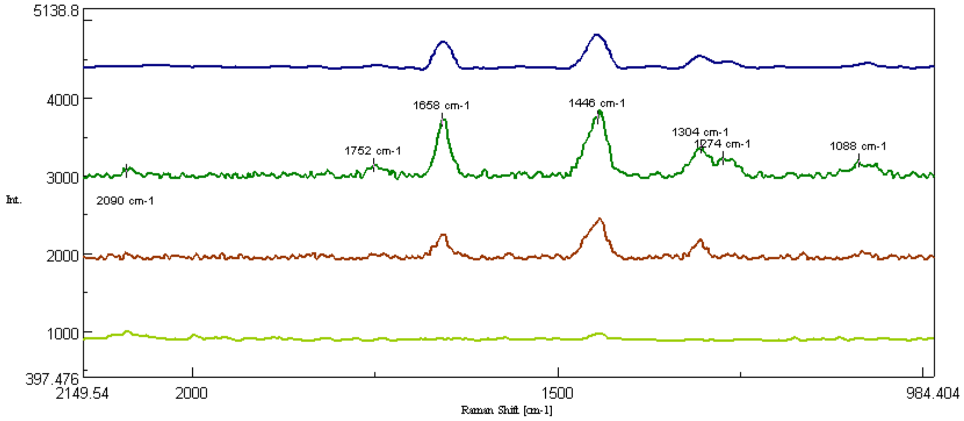

Fig.12. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 2150 cm^{-1} – 980 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of calcium stearate (brown), thickened of aluminium stearate (dark green) and thickened of lithium 12-hydroxystearate-adipate (blue)

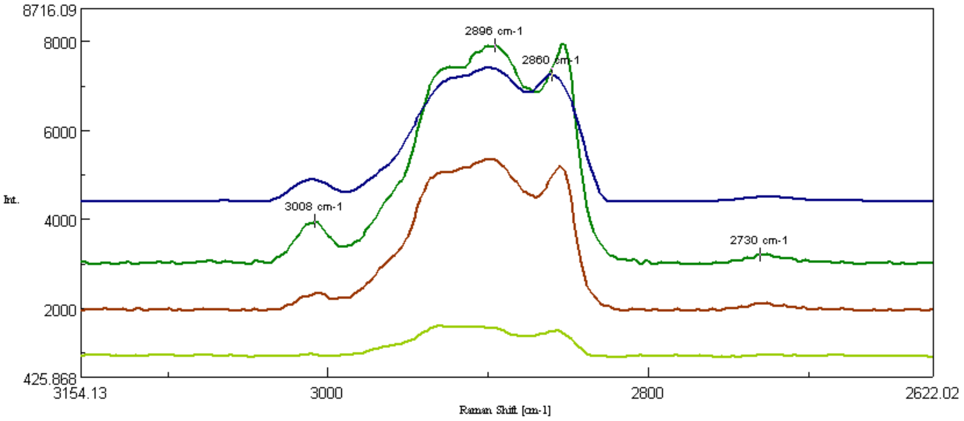

Fig.13. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 3150 cm^{-1} – 2620 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of calcium stearate (brown), thickened of aluminium stearate (dark green) and thickened of lithium 12-hydroxystearate-adipate (blue)

this element (Sb3d) it was found, that antimony was present in the tested layer in the form of sulphates. Proved about this a strong binding energy signal about 525 eV (grease A). Similarly as discussed previously cases, the intensity of this band gradually decreased with the depth of sputtering, until complete disappearance. In the case of nitrogen, in registered XPS spectra of N1s photoelectrons, the 397 eV band (attributable to oxides) was occurred. The analyses showed, that the dominant form, in which nitrogen occurred in the analysed sample were oxides present in the surface layers (greases A,C,D,E,F and G). In the spectra of iron (Fe2p) photoelectrons, a band with 710 eV

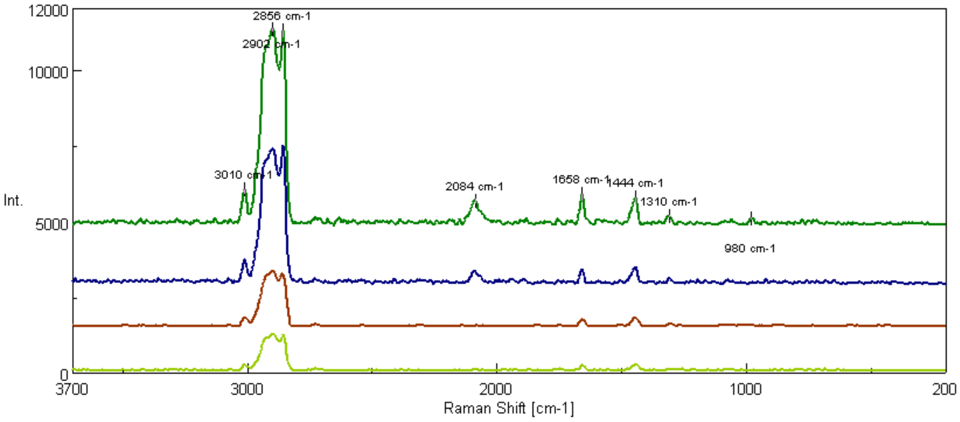

Fig.14. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 3700 cm^{-1} – 200 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of modified Aerosil (brown), thickened of montmorillonite (dark green) and thickened of polytetrafluoroethylene (blue)

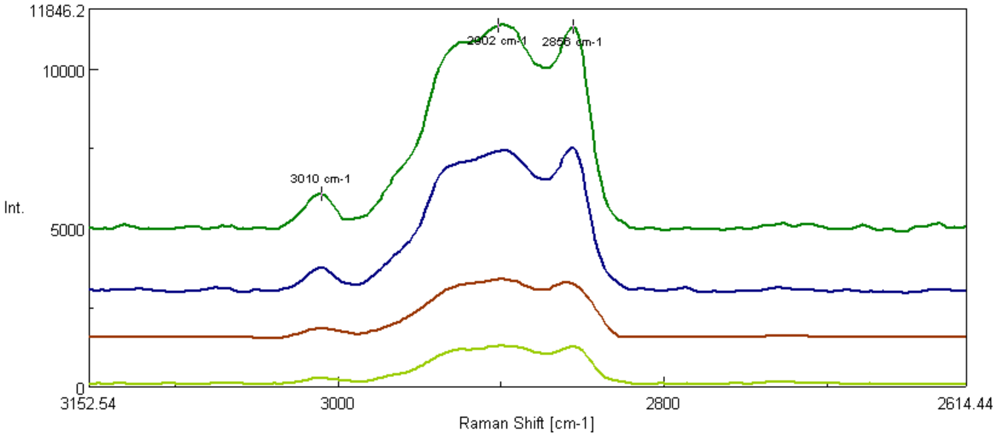

Fig.15. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 3150 cm^{-1} – 2610 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of modified Aerosil (brown), thickened of montmorillonite (dark green) and thickened of polytetrafluoroethylene (blue)

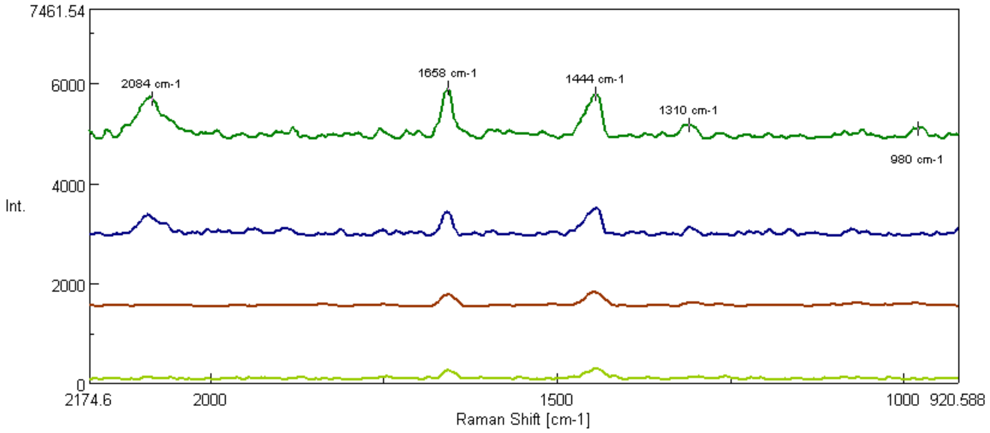

Fig.16. The Raman spectra of tested lubricating greases after tribological tests in the range of the Raman frequency shift 2170 cm^{-1} – 920 cm^{-1}, the greases: thickened of lithium stearate (green), thickened of modified Aerosil (brown), thickened of montmorillonite (dark green) and thickened of polytetrafluoroethylene (blue)

binding energy can be distinguished. This band probably had a complex character and could be composed of signals characteristic of iron in carbides (708.1 eV), oxides (709.7 eV), as well as sulphates and phosphates (711 eV). In the composition of the surface layer after 30 minutes of ion sputtering was not found of the presence of sulphur and phosphorus, while - outside the elements characteristic for steel - oxygen was also present. Would lead to the conclusion, that the iron was also present in the form of oxides (greases A,B,C,D,E,F,G). A similar band analysis as for the iron was carried out for calcium. In the spectra of photoelectrons of this element (Ca2p), a band with binding energy of approx. 350 eV (greases A,B,C,D,E,F,G) was present, derived from calcium in oxides, sulphates and phosphates. This band was recorded in the XPS spectrum only after several sputtering cycles. In the case of silicon, in registered XPS spectra of Si2p photoelectrons, the 102,7 eV band (attributable to oxides and sulphates in grease E) and the 103,5 eV band in greases F, derived from silicon in sulphates, carbides and aminosilicates were occurred. The analyses showed, that the dominant form, in which silicon occurred in the analysed sample were oxides, sulphates and aminosilicates present in the surface layers. In the spectra of photoelectrons of this element (Li1s), a band with binding energy of 55,6 eV (greases A and D) were present, derived from lithium in sulphates and phosphates. This band was recorded in the XPS spectrum only after several sputtering cycles. On the band with 1071,3 eV binding energy, occurring in the spectrum of sodium (Na1s) photoelectrons, may consist of signals characteristic for sulphates and fluorides was present in surface layer of grease G. The XPS spectra of magnesium (Mg1s) photoelectrons (greases B and G) had a characteristic signal of magnesium oxides and sulphates (1304.7 eV) and the magnesium sulphates, phosphates and fluorides (1305,8 eV). This bands disappeared with the depth of sputtering. In the case of aluminium, in the recorded XPS spectra of Al2p photoelectrons there was a bands with 74,4-74,6 eV energy, which quickly disappeared (characteristic for aluminium in oxides, sulphates, fluorides, aminosilicates and phosphates). The carried out analyses showed, that the dominant form in which aluminium was present in the analysed sample were oxides, sulphates, phosphates and fluorides present in surface layers (greases C,F and G).

In conclusion, in the surface layer of the steel wear trace after tribological tests with the involving of mineral greases thickened of different thickeners under friction conditions, the presence of organic and inorganic compounds (i.e. zinc sulphides and phosphates, sulphates, oxides and carbides of the metal components included in the steel and the lithium, aluminium and calcium fluorides, aluminosilicates, silicon sulphates and carbides, lithium sulphates and phosphates, sodium sulphates and fluorides, magnesium sulphates, phosphates and fluorides and aluminium phosphates and sulphates derived from transformation of used thickeners) were found. Together with the depth of sputtering, the amount of inorganic compounds decreased until the complete disappearance of sulphides, phosphates, fluorides and sulphates.

For tested lubricating greases after tribological tests a Raman spectroscopy analyses were performed. The influence of the used thickeners on the chemical structure of lubricants were presented in Fig.11-16. The spectra reveal that on the surface of steel element after tribological tests for mineral lubricating greases containing the various quantity of thickeners, the presence of organometallic compounds in the top layer were recorded. The bands at 3010 and 3008 cm^{-1} was assigned to the -CH group involved in the formation of intermolecular hydrogen bonds of the carbon chain of the used oil base. The bands at 2902, 2895, 2860 and 2856 cm^{-1} were created as a result of overlapping bands characteristic for symmetrical and asymmetric vibrations of the methyl and methylene groups (-CH3, -CH2-) derived from the carbon chain of the oil base of the tested lubricants. The band at 2730 cm^{-1} are derived from the stretching vibrations of the -CH2 and -CH3 groups of the carbon chain. In contrast, the 2090 and 2084 cm^{-1} band is most likely to group stretching vibrations - C=O – characteristic of aerobic oxidation products. The band appearing at 1752 cm^{-1} may be attributed to oscillations of the C=O group characteristic for esters. The band at 1658 cm^{-1} is assigned to the C=C group present in the carbon chain of the oil base. On the other hand, the bands at 1444 and 1446 cm^{-1} can be attributed to the -COO- vibrations or the symmetrical and asymmetric deformations of the -C-H group or groups occurring in this range -C=C-H present in the carbon chain of the oil base and the used thickeners. The bands at 1310, 1304 and 1274 cm^{-1} present in composition thickened of polytetrafluoroethylene is characteristic of the skeletal vibrations of -CF2=CF2- group in the polytetrafluoroethylene. The band at 1088 cm^{-1} is characteristic of the deformation vibrations of the -C-C group in soap thickeners, and at 980 cm^{-1} can be attributed to the deformation vibrations of the -Si-O- group in Aerosil.

The carried out tests showed, that during tribological processes some of the components undergo oxidation, which results in organo-oxygen compounds forming an organic layer on the metal surface, counteracting the wear of the lubricated friction pair. Some compounds come to a close contact with the surface layer, increasing its resistance to wear and shearing. The analysis of the results of rolling contact fatigue tests along with the analysis of the change in the structure of lubricants allows to state that the lubricating properties are not only the effect of the used thickeners but also oxidation products and tribochemical reaction products with the friction pair working surface. The activity of the used thickeners is based on the production (during friction) a thin film strongly chemically bonded to the substrate, characterized by low shear strength and high plasticity and high resistance on the wear processes. As a result of the thermal decay of thickeners, chemical reactions take place between components of the substrate material and greases. The complex compounds penetrate the working surfaces of the friction pair forming layers resistant to wear processes. The boundary layers are formed due oxidation of greases components to polar organic compounds and their interactions with metals or metal oxides. The chemical reactions cause the fragmentation of the hydrocarbon chains of oil base and result in production of polar compounds. The final products of the processes occurring in the friction zone are compounds forming boundary layers on the tribosystem's surface.

In my other works on the influence of lubricants on the rolling contact fatigue of steel tribosystems, the author described in detail the results of fatigue tests in the presence of ecological lubricating greases. In the article [35], the fatigue tests were carried out for lubricating compositions based on vegetable oils, i.e. rapeseed, sunflower, soybean and castor, as well as synthetic (PAO 8) and mineral (paraffinic). The modified silica Aerosil was used as a thickener. The research results obtained in the article are characterized by much lower values of L10 and L50 coefficients than for lubricating compositions based on paraffin oil and thickened with lithium, calcium and aluminum soaps, as well as montmorillonite and polytetrafluoroethylene. In publication [39] the fatigue tests were carried out the compositions based on paraffin, rapeseed and polyalphaolefine oil, thickened with lithium stearate and modified with silica additive. In this case, the results achieved are weaker than in the case of the lubricating compositions discussed earlier. Much higher values of parameters characterizing the level of resistance to fatigue durability were achieved for compositions thickened with aluminum stearate, calcium, montmorillonite or polytetrafluoroethylene. However, in publication [40] describes the results of fatigue stability tests for compositions based on sunflower oil, thickened with lithium stearate and modified with various amounts of polytetrafluoroethylene. The values of the L10 and L50 coefficients characterizing fatigue life are lower for compositions based on vegetable oil than for compositions based on mineral oil. The type of used oil base have a great importance here. The vegetable oils have a much lower resistance on rolling contact fatigue than mineral oils, because the much better results for composition based on mineral oil.

4. Conclusion

The results of the study of rolling contact fatigue were allowed to the conclude, that:

- the used of soap thickeners to produce of lubricating compositions based on the mineral oil were carried out to the reduction in relative to the silica thickeners and polytetrafluoroethylene of values coefficient of L10 and L50, which were characterized the level of resistance of lubricating grease on rolling contact fatigue,
- the used of amorphous silica and montmorillonite as a thickeners of tested lubricating compositions produced on the basis of mineral oil were results an increase in relation to the lithium complex thickener of values of coefficient L10 and L50, which were characterized the level of resistance of lubricating grease on rolling contact fatigue,
- ·the change of the durability fatigue of tested lubricating greases it depends from the chemical structure of the dispersed phase and the interactions between the components of the lubricating composition,
- ·the products of tribochemical reaction between the components of the grease composition and the surface of tribosystem were affected significantly on the value of rolling contact fatigue,
- ·the type of used base oil, and its synergistic or antagonistic interaction of the effects of used thickeners in the tested lubricating compositions has a capital meaning on the value of rolling contact fatigue,
- ·the high effectiveness action of polytetrafluoroethylene thickener was resulted of its low temperature decomposition, and the easier decomposition this the greater improving of durability fatigue,
- ·in the surface layer of the steel wear trace after tribological tests with the involving of mineral greases thickened of different thickeners under friction conditions, the presence of organic and inorganic compounds were found. Together with the depth of sputtering, the amount of inorganic compounds decreased until the complete disappearance of sulphides, phosphates, fluorides and sulphates,
- the analysis of the results of rolling contact fatigue tests along with the analysis of the change in the structure of lubricants allows to state that the lubricating properties are not only the effect of the used thickeners but also oxidation products and tribochemical reaction products with the friction pair working surface. The activity of the used thickeners is based on the production (during friction) a thin film strongly chemically bonded to the substrate, characterized by low shear strength and high plasticity and high resistance on the wear processes.

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