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RESEARCH

# The Tribological and Rheological Properties of Vegetable Lubricating Grease Modified of $TiO_2$ Nanoparticles

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A B S T R A C T

*The article presents the results of tribological and rheological research of lubricating composition modified of various content of titanium dioxide.*

*The analysis of anti-wear properties during the test for the tested lubricating composition indicates a significant change in this parameters for lubricants modified of titanium dioxide. A change of the value of evaluated tribological parameters leads to change in the structure of the composition carried out tests and a change in the effectiveness of the tribological protection of the tribosystem. The content of the thickener, base of oil and additive in the lubricant structure affects the level of the anti-wear properties, as evidenced by the results obtained during the tribological tests presented in this article.*

*Also, the tribological tests were carried out with the T-02 four-ball machine for the base grease, i.e. without a modifying additive, and compared with the results obtained for lubricating greases modified with various amounts of titanium dioxide. The results of welding load, limiting pressure of seizure, scuffing load, limiting load of scuffing and limiting load of wear were used to evaluate the tribological properties. Based on the results of tribological tests of vegetable lubricating compositions, it was found, that the addition of titanium dioxide changed the anti-wear and anti-seizure properties of the vegetable lubricating compositions under study.*

*The introduction of various amount of titanium dioxide caused an increase of dynamic viscosity at lower shear rates and significant changes of viscosity in the low temperatures. The introduction of modifier led to the decrease of yield point value from content value of used additive of tested lubricating compositions.*

## 1. INTRODUCTION

Nowadays, the issue of environmental protection gains growing attention. The EU regulations and policy requires a reduction in the use of environmentally harmful petroleum-based lubricants [1–3]. To manage those requirements, there is a need for lubricating greases that are non-toxic and readily biodegradable. Such components may be obtained from natural sources like vegetable oils, which are increasingly used to produce ecological lubricants [4–8]. The non-toxicity and biodegradability of lubricants are particularly desirable in the applications in devices for the food industry [9,10]. This branch of industry requires the use of lubricants of appropriately selected composition, ensuring their ecological character and thus their neutrality to the natural environment [11–14].

At present, there is a strong demand for lubricating greases based on vegetable oils, combining good lubricating properties with their harmlessness to the environment. There is a tendency to replace petroleum-based lubricants with non-toxic vegetable, readily biodegradable counterparts. The vegetable oils have a very good viscosity-temperature as well as lubricating properties, which determine their suitability as a base for lubricating greases. The major disadvantages of these products are low resistance to hydrolysis, low thermal stability, and susceptibility to oxidation [15–22].

The properties of lubricants depend on their composition and production technology and are shaped, inter alia, by appropriately selected modified additives [23]. Typical packages of additives modified of lubricating greases include, among others, antioxidants (increasing the resistance of the grease to oxidation), anti-wear and anti-seizure additives improving the tribological properties of the product and anti-corrosive (reducing the aggressiveness of the grease towards metals) or adhesive (improving the adhesion of the grease to machine components). Not only the presence of the additive, that determines the working properties of the grease, but also the method of its incorporation into the structure of the grease. The introduction of additives to lubricants causes many technological difficulties, because the additive particles adsorb on the surface of the thickener, which in turn may lead to a reduction in the effectiveness of such a component, and even to a reduction in the stability of the lubricant [23–29]. For lubricants, appropriate, specially selected additives should be used in the amount determining the improvement of their working properties. The lubricating greases mix very well with solid lubricating additives, which reduce the friction force and increase the resistance of the tribosystem to loads and seizure. In difficult working conditions, these additives increase the effectiveness of the lubricant due to its resistance to chemical agents and better resistance to high temperatures. The most frequently used additives are: graphite, molybdenum disulfide, polytetrafluoroethylene, copper and chloroparaffins [24,30-33]. Today, however, the aim is to make lubricants more environmentally friendly and at the same time not to deteriorate their lubricating properties. Due to the increasing role of environmental protection, use lubricants, which do not contain heavy metals, halogens, sulfur or phosphorus [31-33], therefore it was decided to use the non-toxic additive in the form of nanoparticles of titanium dioxide, which have to improve the tribological properties of the tested lubricants. Modern science owes its innovation to nanotechnology, which uses structures having at least one size below 100 nm [34]. The introduction of nanoadditives to the structure of the lubricant significantly improves the antiseizure and anti-wear properties, on which depend the working properties of lubricant compositions. These features explain the great interest in innovative nanoadditives. The negative aspects of the presence of nanoadditives are their high cost, limited availability and difficulties in achieving the appropriate degree of dispersion in the lubricant structure. The proportion of nanoadditives introduced into lubricant compositions at the level of 2-6% is sufficient to achieve specific, high requirements for lubricating greases.

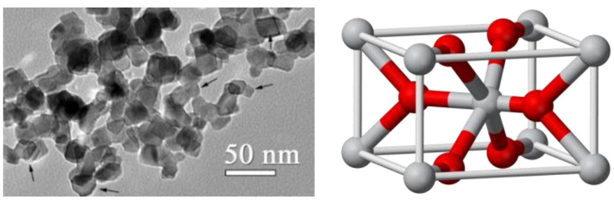


**Fig. 1**. The chemical structure of used nanoadditive (titanium dioxide) [35].

The titanium dioxide ($TiO_2$) (Fig. 1) has become part of our everyday lives. It is found in various consumer goods and products of daily use such as cosmetics, paints, dyes and varnishes, textiles, paper and plastics, food and drugs, and even paving stones. 4.68 million tons of titanium dioxide were produced worldwide in 2009 [36]; 1,5 million tons/year are produced in the European Union [37]. Production was even higher before the financial crisis in 2007 and 2008. The great versatility of titanium dioxide is owing to its various forms and sizes. Titanium dioxides may be used in the form of microscale pigments or as nano-objects. Their crystal structures may vary: depending on the arrangement of $TiO_2$ atoms, one differentiates between rutile and anatase modifications.

Due to its high diffraction index and strong light scattering and incident-light reflection capability, $TiO_2$ is mostly used as white pigment. It is these properties and a high UV resistance that make $TiO_2$ the standard pigment found in white dispersion paints with high hiding power. Since light scattering does not occur anymore in nanoscale particles, the white titanium dioxide pigments used are almost exclusively rutile modification particles with grain sizes in the micrometer range. These white pigments are not only found in paints and dyes but also in varnishes, plastics, paper, and textiles. Having E number E171, they are used as food additives and occur in toothpastes, several other cosmetics, and drugs. $TiO_2$ pigments for use in plastics constitute the fastest growing market. It is in particular due to the packaging industry's strong demand that the consumption of titanium dioxide pigments is on the increase [38].

Nanoscale titanium dioxide that is manufactured for specific applications is by approximately a factor of 100 finer than the $TiO_2$ pigments and has other physical properties. The production volume of nanoscale $TiO_2$ amounts to less than 1 percent that of $TiO_2$ pigments [39]. Unlike $TiO_2$ pigments, nanoscale titanium dioxides are not used as food additives. Currently, they are mainly found in high-factor sun protection creams, textile fibers or wood preservatives. For a long time, suncreams have been manufactured adding titanium oxide microparticles that gave the products a pasty, sticky consistency. Leaving a visible film, application of such suncreams was not easy and not pleasing to the skin. Suncreams that contain the transparent nanoscale titanium dioxides can be applied much more easily. In addition, their protective effect against harmful UV radiation is much better. At present, high sun protection factors can only be achieved using nanoscale titanium dioxides [40].

To achieve better dispersion properties and ensure photostability, these $TiO_2$, moreover, are coated with further materials [41]. The photocatalytic activity, which is another property of $TiO_2$, is increased considerably through the high surface-to-volume ratio of the nanoparticles as compared to that of microparticles. However, not each of the above modifications can be used for photocatalytic purposes. While, as has been shown above, rutile $TiO_2$ are applied mainly in suncreams, paints, and dyes, anatase modifications are rather suited for photocatalysis. In the presence of UV radiation, anatase $TiO_2$ can form radicals from air or water which can degrade oxidatively organic pollutants [42].

Due to the hydrophilic character of titanium dioxide, water forms a closed film on the surface in which pollutants and degradation products can be easily carried away. House paints or tiles containing $TiO_2$ particles thus are self-cleaning and pollutant-degrading. Besides, so-called anti-fog coatings benefit from the hydrophilic properties of nanoscale titanium dioxide. The ultra-thin water film on a glass pane coated with a transparent layer of nanoscale $TiO_2$ impedes the formation of water droplets and, thus, avoids fogging. Nanoscale titanium dioxides are also suited for use in dye-sensitized solar cells (Graetzel cells) [40].

Based on what we know metal nanoparticles, oxide nanoparticles and hydrate nanoparticles can change their oil solubility utterly under the effect of surface modification—even transfer from water to oil phase [37,38]. However, titanium (Ti) atoms of $TiO_2$ coordinate with either two or three oxygen atoms (O) to form $TiO_2$ or $Ti_2O_3$ groups, so they are hybridized to a planar or three-dimensional structure. Such structure units can comprise several different typical groups through various combinations, which lead to a structure more complex and cause the difficulty of surface modification of $TiO_2$. However, the transfer and adhesion of the nanoparticles accelerates surface modification, self-reduction, and the formation of a fine $TiO_2$

tribofilm that reduced the coefficient friction, pressure, and temperature in contact area and hence wear. Thus, it can be concluded that both methods (listed above) are classical and have their own defects (the addition of dispersant or usage of surfactant into base oil) for solving the oil solubility of $TiO_2$ nanoparticles. This claim is strengthened by the works of several researchers [42-47]. Therefore, the application process of the two classical methods was named the traditional process (TP). The $TiO_2$ nanoparticles cannot be well dispersed in the base oil after the TP, for the sedimentation is unavoidable in time, with negative effect on tribological properties.

The aim of this work was the analysis of various quantity of titanium dioxide in vegetable grease on change of tribological and rheological parameters for the lubricating compositions applicable in the food industry.

## 2. THE METHODOLOGY OF RESEARCH

To the tribological tests was used the lubricating composition, which was prepared using the non-toxic ingredients, that are a dispersing and dispersed phase [48-51]. As a dispersing phase, the vegetable oil with very good physicochemical properties was used. The linseed oil, which was used in tribological tests, is characterized by the following physicochemical properties: 0.876–0.898 g/cm$^3$ density; 46.33 cSt kinematic viscosity at 40°C; 2.11 meq $O_2$/kg peroxide number; 81.22 g $I_2$/100 g iodine number; 160.44 mg KOH/g saponification number; and 0.21 mg KOH/g acid number. The linseed oil consists of over 40% of erucic acid (C22-1), which determines its qualities. It is an ultra-light oil, has a low viscosity, high absorbability, very good antioxidant properties, and characterized of excellent sliding, very good lubricating properties and high chemical resistance [52-54,55].

The following lubricating greases were used for the tests: based on linseed oil and thickened with lithium stearate (grease A), modified with 1% of titanium dioxide (grease B), modified with 2% of titanium dioxide (grease C), modified with 3% of titanium dioxide (grease D) and modified with 5% of titanium dioxide (grease E). The lubricating compositions thus prepared were then marked with the symbols A, B, C, D and E. The lithium stearate was used as the dispersed phase. In the early phase of the experiment, research was carried out on the amount of the thickener that should be incorporated into the lubricating composition.

The lithium stearate used as a thickeners was introduced to the vegetable base oil in an amount of 8% m/m. The lubricating composition prepared in this way were subjected to tribological tests.

To determine the tribological (anti-wear) properties of the tested lubricating composition, was used a compact MCR 102 rotational rheometer of the Anton Paar company with tribological cell T-PTD 200 (Fig. 2.) with a concentric plate-ball contact point, in which three fixed cuboid steel plates were pressed with adequate force through a ball fixed in the spindle, rotating at the appropriate speed.

**Fig. 2.** The rotational rheometer MCR 102 with tribological cell T-PTD 200 [55].

The tribological device enables the execution of tests in the temperature range of -40÷200°C. The balls with a diameter of 12.7 mm and plates with dimensions of 15 × 5 × 2 mm were made of bearing steel LH 15 (Ra = 0,3 µm; hardness 60–63 HRC). During the tests, immersion lubrication was used. Tribological tests (measurement of limiting load of wear - LLW) were carried out at the tribosystem at 10.00 N, rotational speed of 500 rpm, during 3600 s and temperature of 20$^o$C. The parameters i.e. friction factor, friction work, frictional force and frictional power were also measured during the experiment. Before starting the tribological attachment, the plates were placed in the holder, pressed with springs, lubricant was introduced (approx. 5 cm$^3$) and stabilized for 60 s at a set temperature. During the test, the tribological parameters was recorded, which was automatically converted into a coefficient of friction at 36-second intervals. Three test runs were performed, and the final test results were averaged. The final result of the run was the value of 100 measurements registered during the test.

The averaged results obtained during the tests were also given. For statistical processing of the results, the Q-Dixon test was used with a confidence level of 95%. After testing, the components of the tribosystem were dismantled, washed with n-hexane and dried.

The limiting load of wear is a measure of the anti-wear properties of the lubricating composition. The determination of this parameter consisted in calculating its value in accordance with the formula (1):

$$LLW = 0.52 * LT/d_{LW^2} \quad (1)$$

where, LT–load of the tribosystem equal to 10.00 N, and $d_{LW}$-the diameter of the diathesis formed on the steel plates used for the test.

The optical microscope was used to determine the size of the trace of wear of the surface of rectangular test plates. The obtained results were used to determine the size of LLW, i.e. the evaluation of anti-wear properties of lubricating composition subjected to tribological tests [52-53,56].

The friction factor value are calculating in accordance with the formula (2):

$$\mu = F_R/F_L \quad (2)$$

where, $F_R$ –friction force, $F_L$-normal load.

The friction force are calculating with the formula (3):

$$F_R = M/r * sin\alpha \quad (3)$$

where, M – torque, r- radius of friction force.

While the normal load are calculating with the formula (4):

$$F_L = F_N/cos\alpha \quad (4)$$

where, $F_N$-normal force.

The sliding speed are calculating with the formula (5):

$$v_S = 2\pi/60 * n * r * sin\alpha \quad (5)$$

where, r- radius of friction force, n- number of rpm, and sliding distance (6):

$$S_S = \varphi * r * sin\alpha \quad (6)$$

where, r- radius of friction force, φ – correlation coefficient [56].

**Fig. 3.** The T-02 tribological tester.

The tribological properties of the lubricating compositions were evaluated on a T-02 of four-ball machine (Fig. 3). These properties were determined by measuring of welding load (WL), scuffing load (SL), limiting load of scuffing (LLS), and limiting pressure of seizure (LPS). The friction pair to be tested elements was the steel balls of diameter 12.7 mm, applied in steel bearing type LH 15. The roughness of ball surface was Ra = 0.32μm and its hardness was 60-65HRC. The welding load was evaluated according to PN-76/C-04147. This test was carried out in a 10-second runs of four-ball machine in the presence of the lubricant under increasing load until the balls welded. The measurements of lubricating properties in scuffing conditions (i.e. in the constantly increasing load during the tests) were carried out according to the methodology developed by the tribology scientists. The test was performed in a linearly increasing load from 0 to 7200 N (ramp 409 N/s) within the time of 18 s at 500-rpm spindle speed. The moment of a sudden increase of the friction point is called the scuffing load SL. The measurement was carried out until the point of friction reached the point of 10 Nm or the maximum load of device set up at 7200 N. This point was defined as the limiting load of scuffing LLS. The result of each test was determined as an arithmetic average of at least three separate measurements, which did not different from one another more than 10%. The Q-Dixon test at the 95% trustfulness level was used for statistical processing of results. The limiting pressure of seizure is a measurement of the antiscuffing properties of lubricants in scuffing conditions. The estimation of this parameter was based on a calculation according to the formula (7):

$$LPS = 0.52 * LLS/d_{LS^2} \quad (7)$$

where, LLS – limiting load of scuffing and $d_{LS}$ – scar diameter formed on the steel balls used in the tests.

To determine the size of the wear scar on the surface of tested balls, an optical microscope was used. The obtained results were used to determine the size of LPS, or the estimation of antiscuffing properties of lubricating greases subjected to tribological tests [52,53].

**Fig. 4.** The rotational rheometer MCR-101 Anton Paar with air bearings.

The MCR-101 rotational rheometer with Anton Paar, equipped with a diffusion air bearing, connected to pneumatic power supply - an oil-free Jun-Air compressor and an air-drying block was used to determine the rheological properties of the tested lubricants (Fig. 4). The device was equipped with Peltier temperature control system in the range -40-200°C and in the external VISCOTHERM V2 thermostatting system, operating in the temperature range -20-200 °C. The rheometer is controlled and the measurement data is analyzed using the Rheoplus software. The measurements were made using a cone-plate measurement system. For the selected measuring system, the zero gap was set at the test temperature. This procedure is performed automatically by the camera. After setting the zero gap in the center of the plate, the sample is placed in such an amount that the entire amount of the sample is evenly distributed over the surface of the cone after lowering the head with the cone to the measuring position. Then the test temperature was set. It was decided to perform tests at a temperature of 20$^{o}$C. Then, the shear rate range was set in which the tests will be carried out (0.01 - 100 $s^{-1}$) and the measurement intervals in which data are collected (number of measurement points, total measurement duration and data collection frequency). For viscosity curves were carried out in temperature range -30-180$^{o}$C and range of shear rate 0-1000 $s^{-1}$. When measuring the flow curves, a logarithmic curve was used to collect more points at the beginning of the range, which is decisive in determining the min. flow limit. The tests were carried out for lubricating compositions prepared on vegetable oil with different content of titanium dioxide [50,52,54].

## 3. THE RESULTS OF TRIBOLOGICAL RESEARCH

For tested vegetable lubricating greases was carried out the tribological properties, and then the evaluation tribological parameters of tested lubricating composition. The obtained test results are shown in Figs. 5-9 and Table 1.

**Table 1.** The calculated tribological parameters of tested lubricating greases.

| Tribologcal parameters | A | B | C | D | E |
|---|---|---|---|---|---|
| The limiting load of wear LLW [N/mm$^2$] | 428,58 | 498,16 | 606,26 | 748,45 | 468,43 |
| The average friction coefficient [-] | 0,153 | 0,119 | 0,094 | 0,056 | 0,088 |
| The welding load WL [N] | 1569,6 | 1569,6 | 1962,0 | 2452,5 | 1962,0 |
| The limiting pressure of seizure LPS [N/mm$^2$] | 305,71 | 332,41 | 356,60 | 545,63 | 375,62 |
| The scuffing load SL [N] | 1300 | 1500 | 1800 | 2200 | 1900 |
| The limiting load of scuffing LLS [N] | 3500 | 3900 | 4100 | 4500 | 4300 |

The tribological tests of lubricating compositions produced on vegetable base oil and modified of titanium dioxide showed, that the used modifying additive has a positive effect on changes of the friction coefficient and the ability of obtained lubricants to anti-wear protection of the tribosystem in comparison to the compositions produced on different oil bases and modified with classical and non-classical additives [57-59]. For the grease A, which did not include in its composition the modified additive, the stable friction coefficient values was observed. It weren't observe a significant changes in this parameter during the tribological test. During the measurement, the friction coefficient ranged between 0.12-0.18 [-]. The grease composition (B), which has been modified by introducing 1% of titanium dioxide was characterized by more stable friction coefficient values. It was observed the lower values of this parameter than for grease A, which didn't contain the additive in its composition, which confirms the belief in the effectiveness of the used additive. The changes of the friction coefficient over time range from 0.10-0.14 [-], which suggest that, the titanium dioxide was sufficiently homogenized in the grease structure. The Table 1 shows, that for grease C, which has been modified of 2% of used additive, the value of friction coefficient was much lower in comparison to the composition A, which was not modified of titanium dioxide. In this case, the value of the friction coefficient stabilizes at the level of 0.09-0.10 [-]. For the composition being discussed obtained clearly better results than for composition A without a modifier. For this composition very good homogenization of the additive was achieved in the structure of the grease, which is evidenced by stable friction coefficient values during the test. However, the composition D, which has been modified with 3% of titanium oxide was characterized by very stable and lower friction coefficient values. In this case, the value of friction coefficient it ranged in terms of 0.04-0.06 [-]. Such stable and lower values of this parameter for this composition may be caused by even distribution of the modifying additive in the structure of tested lubricant. The average friction coefficient for this composition was the lowest of all tested lubricating compositions. The introduction of this amount (3%) of the additive ($TiO_2$) to the grease structure works very effectively, which determines the effective protection of machine and device elements against wear. The grease E, which was modified of 5% of additive characterized by the average value of friction coefficient amounting to 0.07-0.11 [-]. In the initial phase, the value of the discussed parameter was quite high and was at the level of 0.14 [-], later it dropped to 0.07 [-] to increase again to 0.09-0.12 [-]. In the further phase of the test, the value of the friction coefficient ranged from 0.08-0.10 [-]. It was observed high changes of friction coefficient for this composition. Such high changes of this parameter are unacceptable, because it may cause the impossibility of effective protection against damage to machine and device elements.

Therefore, the lubricating compositions containing 1-3% of titanium dioxide characterized by a lower value of friction coefficient, more lower than the initial composition and stable changes of this parameter over time determine the very effective tribological protection against wear.

The results of tribological tests (anti-scuffing and anti-wear properties) of lubricating greases based on a vegetable oil base and modified with various amounts of titanium dioxide are presented below. The welding load WL were determined for the selected grease compositions. The obtained results are shown in Fig. 5.

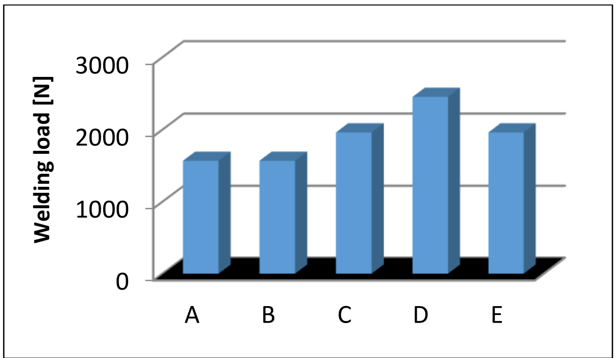


**Fig. 5.** Welding load of tribosystem lubricated compositions with various amount of additive.

The evaluation of the anti-scuffing properties with the abruptly increasing load of the tribosystem showed a favorable effect of the applied modifier on the durability of the lubricating film (Fig. 5). The most advantageous anti-scuffing properties are characterized the grease prepared on a vegetable base and modified with 3% of titanium dioxide - an increase of the WL value by 56% in compared to the basic composition, which was not modified with the applied additive. The lubricating compositions modified with 2% and 5% of titanium dioxide, respectively, did not show such favorable changes of anti-scuffing properties as composition D, although there was a noticeable improvement in anti-scuffing properties in compared to the basic composition without the modification additive (increase of the WL parameter by 25% in compared to the composition without the modifier). For the lubricating composition modified with 1% additive, no changes of the tested parameter in relation to the basic composition were noticed. The modifier used in the amount of 2-5% in vegetable lubricants allows for the improvement of anti-scuffing properties with the abruptly increasing load of the tribosystem, although it does not create highly resistant to scuffing layers, that significantly increase the durability of the lubricant film for the tested lubricating compositions.

The measure of the anti-scuffing properties of the tested lubricating compositions under seizure conditions is the limiting pressure of seizure. The obtained results of testing this parameter are shown in Fig. 6.

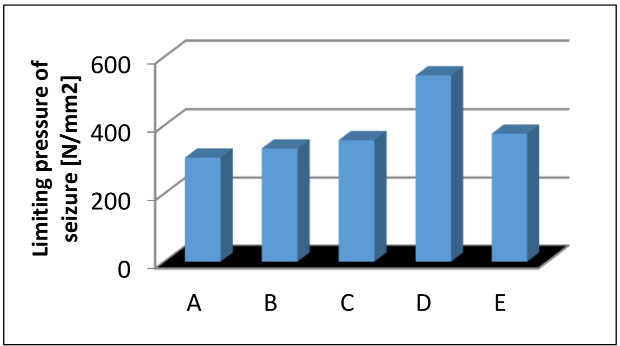


**Fig. 6.** Limiting pressure of seizure of tribosystem lubricated compositions with various amount of additive.

The most advantageous anti-scuffing properties under seizure conditions are characterized the vegetable-based lubricant modified with 3% of titanium dioxide. In this case, an increase of the LPS value about 78.7% was observed in compared to the basic composition without the modifying additive. Lubricating compositions prepared on vegetable oil and modified with 1% and 2% of titanium dioxide did not show such favorable changes in anti-scuffing properties as composition D modified with 3% of additive (Fig. 6). Similarly to the composition E, which was created by introducing a 5% of modifier into the structure of the base lubricant. The determined values of the limiting pressure of seizure showed, that the use of titanium dioxide as a modifier of the tribological properties of vegetable lubricating greases positively influenced on the improvement of anti-scuffing properties of the lubricant compositions used in the experiment. The application of 1-2% and 5% of $TiO_2$ as a modifier of tribological properties improves the anti-scuffing properties in relation to the basic lubricant composition, but the introduction of 3% of the modifier to the structure of the lubricant shows the most favorable anti-scuffing effect, which increased the surface layer's resistance to seizure. The LPS parameter provides the information about the pressure in the friction zone at the time of seizure. On the basis of the obtained results, it can be concluded, that the most of the tested lubricating greases modified of titanium dioxide do not create the highly resistant to scuffing surface layers. The higher LPS parameter in the case of composition modified of 3% additive indicates, that the nature of the created film favors a significant reduction of wear.

For all prepared lubricant compositions, the anti-scuffing properties were determined under conditions of linearly increasing load, characterized by the scuffing load SL. The obtained results are shown in Fig. 7.

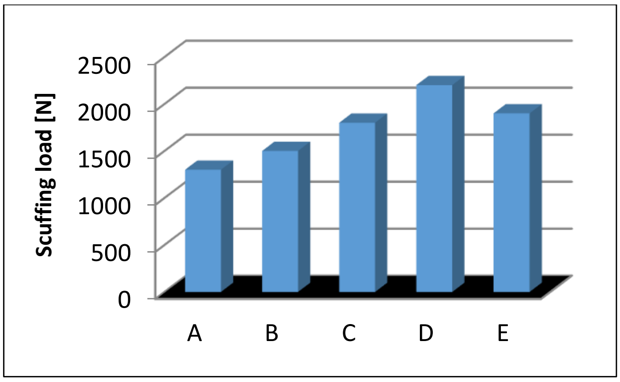


**Fig. 7.** Scuffing load of tribosystem lubricated compositions with various amount of additive.

The scuffing load determines the level of anti-scuffing properties of the tested lubricants under conditions of linearly increasing load. The properties characterized by the SL parameter determine the capacity of the lubricating film to the transferring loads. The most advantageous anti-scuffing properties in conditions of linearly increasing load is characterized by grease produced on the vegetable oil base and modified with 3% of titanium dioxide. An increase value of the discussed parameter about 69.2% in relation to the basic composition without the modifying additive was observed. An increase the SL value respectively about 15.4% and 38.5%, for grease B and grease C modified with 1% and 2% of titanium dioxide, in compared to the base composition, were observed. The weaker scuffing properties in conditions of linearly increased load is characterized grease with vegetable base oil and modified of 5% additive. In this case, the SL value increased about 46.2% in compared to the basic composition, was observed (Fig. 7). The highest durability of the lubricating film provides the application of titanium dioxide as a modifier of tribological properties in the amount of 3%, which allows to obtain a lubricant with the highest SL value. It may therefore be assumed, that the anti-scuffing effectiveness will depend on the boundary layer structure formed by the used modifier in appropriate amount. In the lubricant composition modified with 3% of the additive, the individual particles of titanium dioxide in the lubricating film are more closely packed, which increases their mutual interactions, and thus increases the resistance of the lubricating film to transfer larger loads.

The limiting load of scuffing of tribosystem lubricated with the tested lubricating compositions was also determined. The obtained results are presented in Fig. 8.

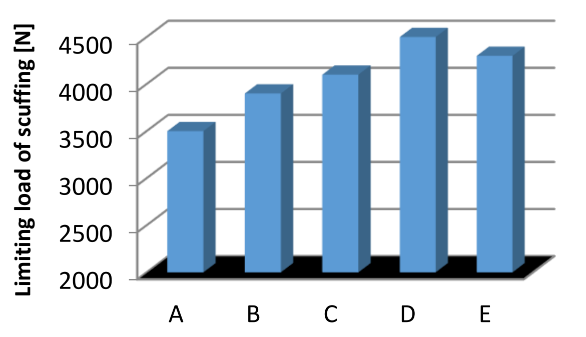


**Fig. 8.** Limiting load of scuffing of tribosystem lubricated compositions with various amount of additive.

The limiting load of scuffing allows to determine the level of anti-scuffing properties of the tested lubricants. The most advantageous anti-scuffing properties is characterized the grease produced on vegetable base oil, that has been modified with 3% of titanium dioxide. For this composition, an increase of the LLS value of 28.6% was observed in compared to the base composition without the modifier. The greases which have been modified with 1% (grease B) and 2% (grease C) of titanium dioxide have weaker protection against seizure. In these two cases, an increase of the value of LLS respectively about 11.4% and 17.1%, in compared to the base composition based on vegetable oil, were observed. The lubricating compositions prepared on vegetable oil and modified with 1-2% and 5% of applied additive - titanium dioxide did not show such favorable changes of anti-scuffing properties as the composition modified with 3% of the modifier (Fig. 8). The most effective way of the lubricant after breaking the lubricating film ensures the application of 3% titanium dioxide, which allows obtaining the lubricant with the highest value of LLS. The LLS values are in the range of 3500–4500 N, which may indicate, that the differences in the composition of lubricants play an important role only under moderate forces. During the seizure process, the increasing pressure in the friction zone causes, that there is no lubricating film on the cooperating surfaces. The protective effect against the immobilization of the tribosystem can be provided by the additive of titanium dioxide in an appropriate amount, which can react with the material of the friction pair. The effect of this is reduce the possibility of formation of adhesive tacks.

The anti-wear properties of the tested lubricating greases were verified by determining the limiting load of wear LLW of the tribosystem lubricated with the evaluated compositions. The obtained results are presented in Fig. 9.

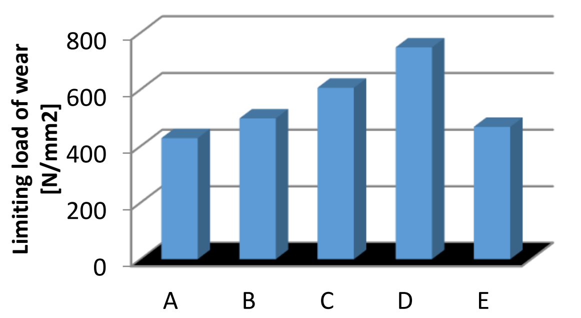


**Fig. 9.** Limiting load of wear of tribosystem lubricated compositions with various amount of additive.

The research of the lubricating properties of produced lubricants showed, that the titanium dioxide introduced into the lubricants' structure changed the ability of vegetable lubricants to protect the tribosystem against wear. The modified lubricating greases were characterized by different values of determined LLW index in relation to the base grease. Each quantity of titanium dioxide introduced into the structure of the basic vegetable lubricant had a positive effect on their anti-wear properties (Fig. 9). After testing each of the produced lubricants, less wear of the tribosystem were observed, than after testing the basic composition (without the modifier). The durability of the boundary layer is confirmed by the value of limiting load of wear LLW. The higher this index, the greater the durability of the boundary layer and the lower of wear. The best anti-wear properties is characterized by the vegetable lubricant, which has been modified with 3% of titanium dioxide (grease D) - an increase of the LLW parameter value about 74.8% in relation to the composition without the modifier. The weaker anti-wear properties is characterized by the vegetable grease modified with 2% of titanium dioxide – an increase of the LLW value about 41.6%, and modified 1% of additive – an increase of the LLW value about 16.4% in compared to the basic composition. The weakest effect of titanium dioxide was observed for the composition modified of 5% additive - an increase of the LLW value about 9.3%. The optimal value of additive introduced into the structure of vegetable lubricating grease is 3%, because it allows to obtain a grease with the highest anti-wear protection. The higher concentration of additive causes the deterioration of the anti-wear properties of the tested lubricating compositions.

It was found that, the use of titanium dioxide as a modifying additive in the tested lubricant compositions has a positive effect on their anti-wear properties. All modified of additive compositions guarantee effective anti-wear protection of the tribosystem under constant load conditions. The content of additive in the lubricant structure affects the level of their anti-wear properties, as evidenced by the results obtained during the tribological tests presented in this article. The highest resistance to wear was noted for lubricants containing 3% of modifying additive, which was reflected in the results of the LLW parameter test.

The tests conducted have shown that the introduction of a modifying additive to the lubricating compositions significantly changes the internal structure of the tested lubricants. The reason for this is the chemical structure of the additive used.

The quality criteria for lubricants, especially for the food industry, are determined individually by machine manufacturers. As a result of the market analysis, it can be concluded, that the lubricant compositions with a LLW parameter > 600 $N/mm^2$ are characterized by very good anti-wear properties, and those with a limiting load of wear in the range of 400-600 $N/mm^2$ provide the effective anti-wear protection, while if LLW < 400 $N/mm^2$, then we speak of insufficient anti-wear properties.

## 4. THE RESULTS OF RHEOLOGICAL RESEARCH

For selected lubricating compositions were carried out the tests of rheological properties on the rotational rheometer. The influence of various amounts of the modified additive on the rheological properties of lubricating greases were presented on Figs. 10-13. The calculated value of rheological parameters for tested lubricating greases were presented in Table 2 and Table 3.

To describe the flow curves of the tested lubricating compositions, two rheological models were used: Casson and Herschel-Bulkley.

The Herschel-Bulkley model it's the easiest model to describe the flow curves of non-linear plastic-viscous fluids [60-62]:

$$\tau = \tau_0 + k * \gamma_n \tag{8}$$

where:
$\tau$ – shear stress [Pa],
$\tau_0$ – yield point [Pa],
$k$ – the consistency coefficient [$Pa*s^2$],
$\gamma$ – shear rate [$s^{-1}$],
$n$ – the flow index [-]

The Casson model describes the flow curves of nonlinear plastic-viscous fluids and is as follows [63-65]:

$$\tau^{1/2} = {\tau_0}^{1/2} + (n_\infty * \gamma) \tag{9}$$

where:

τ – shear stress [Pa]

$\tau_0$ – yield point [Pa]

$\eta_\infty$ - the structural viscosity of grease [Pa*s]

γ – shear rate [1/s].

**Table 2.** The calculated rheological parameters of tested lubricating greases: (a) Cassson model, b) Herschel-Bulkley model.

(a)

| The tested grease | The Casson model | | |
|---|---|---|---|
| | The determination coefficient $R^2$ [-] | yield point $\tau_0$ [Pa] | The structural viscosity $\eta_\infty$ [Pa*s] |
| A | 0.954 | 714,23 | 9.12 |
| B | 0.968 | 234.64 | 7.92 |
| C | 0.980 | 189.12 | 7.36 |
| D | 0.998 | 89.73 | 6.44 |
| E | 0.999 | 72.67 | 6.08 |

(b)

| The tested grease | The Herschel-Bulkley model | | |
|---|---|---|---|
| | The determination coefficient $R^2$ [-] | yield point $\tau_0$ [Pa] | The consistency coefficient k [Pa*s$^2$] |
| A | 0.976 | 654.77 | 15.54 |
| B | 0.982 | 213.34 | 8.65 |
| C | 0.994 | 176.85 | 5.32 |
| D | 0.999 | 84.38 | 3.48 |
| E | 0.999 | 68.52 | 3.11 |

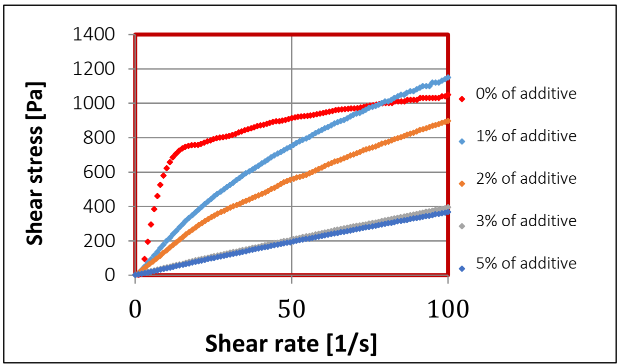


**Fig. 10.** The flow curves of lubricating greases modified of various content of titanium dioxide.

On the rheological properties of lubricating greases a great influence have a type of base oil and thickener, as well as the type and concentration of the additive introduced into the grease, and also the production technology and the conditions in which the grease is used. The interaction between the thickener and additive particles increases with increasing the percentage of additive. With the increase of this participation, the value of the structural viscosity and the yield point in the lubricant is changing. The lubricant production temperature and the cooling intensity during the lubricant production process have a significant impact on the stability of the lubricant structure and the shaping of the value of the shear stress. In order to strengthen this structure and make it more homogeneous and resistant to external factors, is used additives which, to the required extent and degree, modify the free interfacial energy between the base oil and the individual thickener particles. The particles of thickeners or additives of lubricating greases, which are essentially colloidal solutions, have the dimensions of one micrometer or are slightly smaller, therefore the addition of nanometric titanium dioxide significantly influences the changes of the rheological properties the tested lubricant compositions.

The value of the ultimate shear stress (yield point) decreases with the increase of the percentage content of the modifying additive until a certain optimum is reached. This proves, that the introduction of the modifier to the lubricant does not weaken but strengthens its spatial structure. It is important role for the selection of construction parameters when designing the central lubrication system with lubricating grease compositions with the addition of titanium dioxide.

The evaluation of the yield stress using the Herschel-Bulkley model and using of linear regression allowed to obtain lower yield strength values than the results obtained with the Casson model with a fairly high correlation coefficient. The obtained results of the flow curves allow for the conclusion, that the rheological properties (yield point) of the tested lubricant compositions changed significantly depending on the amount of used modifying additive. Modifying the vegetable lubricants with titanium dioxide reduces their yield point. The magnitude of changes of the yield point value depends on the chemical structure and physicochemical properties of the base oil, shaped by intermolecular interactions - mainly van der Waals forces, and the amount of the modifying additive.

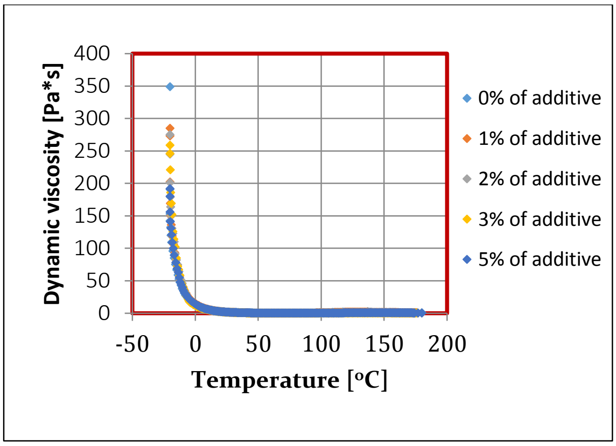


**Fig. 11.** The viscosity curves of lubricating greases modified of various content of titanium dioxide.

The introduction of increasing amounts of modifier into the grease caused an decreased of dynamic viscosity at lower temperature values. The introduction of 3 % of titanium dioxide into the lubricating composition revealed a significant increase of dynamic viscosity at higher temperature in compared to the basic grease. Assessing changes of dynamic viscosity in temperature for the tested lubricating compositions it should be noted, that the introduction of titanium dioxide into the structure of greases caused a minimum changes of viscosity in wide range of temperature.

The introduction of increasing amounts of modifier into the grease caused a significant changes of dynamic viscosity at lower shear rate values. The introduction of 1% of titanium dioxide into the lubricating composition practically has not changed the dynamic viscosity at the lower value of shear rate. With the content of 2% of modifier to the structure vegetable grease was observed change of dynamic viscosity about 23% in compared to the basic grease without the additive.

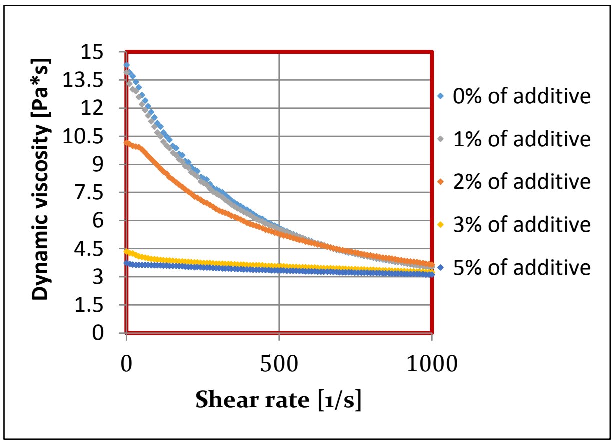


**Fig. 12.** The viscosity curves of lubricating greases modified of various content of titanium dioxide

The minimum value of dynamic viscosity at the lower values of shear rate were observed in cases greases, which were modified of 3% and 5% of titanium dioxide. The value of dynamic viscosity of the tested lubricating compositions decreased along with the increasing amount of additive in lower values of shear rate. The lowest viscosity was observed for the grease modified with 5 % of titanium dioxide, and the higher for grease modified of 1% of modifier.

The size of surface area of the loop hysteresis, i.e. between the flow curve with increasing shear rate and the flow curve with decreasing shear rate, was calculated using the integral method. The obtained values were used to determine the thixotropic properties of the tested lubricants [66].

**Table 3.** The calculated value of surface area of loop hysteresis of tested lubricating greases.

| The tested grease | The value of surface area of loop hysteresis [Pa] |
|---|---|
| A | 372.43 |
| B | 74.16 |
| C | 256.86 |
| D | 556.82 |
| E | 71.74 |

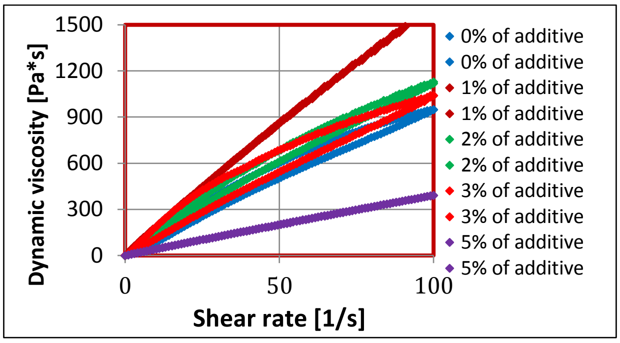


**Fig. 13.** The hysteresis loop of lubricating greases modified of various content of titanium dioxide

Thixotropy is a process in which the internal structure of the lubricant is damaged, resulting in a reduction of its viscosity with the over shear time, as well as the slow process of rebuilding the lubricant's structure to its original consistency. The area of the hysteresis loop is a measure of the thixotropy of the lubricant. The mechanism of thixotropy is related to the phenomenon of shear thinning. The phenomenon of thixotropy can be explained as a result of the aggregation of thixotropic fluid particles. When such a lubricant is at rest, the agglomeration of the particles gives rise to the internal structure of the suspension. If the grease is subjected to shear, the produced structure may be partially or completely disintegrated. After some time, an equilibrium is established, defining a new state of the intermolecular bond network in lubricants. All the tested vegetable lubricants modified with titanium dioxide in different degree showed the phenomenon of thixotropy, visible as the lack of overlapping of the flow curves obtained at increasing and decreasing shear rates. The values of the hysteresis loop surface areas of the tested lubricants are showed in Table 3. The highest value of the thixotropy hysteresis surface was observed in vegetable lubricant modified with 3% of titanium dioxide, while the lowest value was observed in the modified lubricant with 5% of used additive. The most effective action of the additive was observed for composition D, which restored the damaged structure most quickly.

## 5. CONCLUSION

The carried out tests showed different influence of used modifying additive on changes the tribological and rheological properties of tested lubricating compositions.

The tribological tests of lubricating compositions produced on vegetable base oil and modified of titanium dioxide showed, that the used modifying additive has a positive effect on changes of the friction coefficient and the ability of obtained lubricants to anti-wear protection of the tribosystem.

The lubricating compositions containing 1-3% of titanium dioxide characterized by a lower value of friction coefficient, more lower than the initial composition and stable changes of this parameter over time determine the very effective tribological protection against wear.

The modifier used in the amount of 2-5% in vegetable lubricants allows for the improvement of anti-scuffing properties with the abruptly increasing load of the tribosystem, although it does not create highly resistant to scuffing layers, that significantly increase the durability of the lubricant film for the tested lubricating compositions.

The LPS parameter provides the information about the pressure in the friction zone at the time of seizure. On the basis of the obtained results, it can be concluded, that the most of the tested lubricating greases modified of titanium dioxide do not create the highly resistant to scuffing surface layers. The higher LPS parameter in the case of composition modified of 3% additive indicates, that the nature of the created film favors a significant reduction of wear.

The highest durability of the lubricating film provides the application of titanium dioxide as a modifier of tribological properties in the amount of 3%, which allows to obtain a lubricant with the highest SL value. It may therefore be assumed, that the anti-scuffing effectiveness will depend on the boundary layer structure formed by the used modifier in appropriate amount. In the lubricant composition modified with 3% of the additive, the individual particles of titanium dioxide in the lubricating film are more closely packed, which increases their mutual interactions, and thus increases the resistance of the lubricating film to transfer larger loads.

The most effective way of the lubricant after breaking the lubricating film ensures the application of 3% titanium dioxide, which allows obtaining the lubricant with the highest value of LLS. The LLS values are in the range of 3500–4500 N, which may indicate, that the differences in the composition of lubricants play an important role only under moderate forces. During the seizure process, the increasing pressure in the friction zone causes, that there is no lubricating film on the cooperating surfaces. The protective effect against the immobilization of the tribosystem can be provided by the additive of titanium dioxide in an appropriate amount, which can react with the material of the friction pair. The effect of this is reduce the possibility of formation of adhesive tacks.

It was found that, the use of titanium dioxide as a modifying additive in the tested lubricant compositions has a positive effect on their anti-wear properties. All modified of additive compositions guarantee effective anti-wear protection of the tribosystem under constant load conditions. The content of additive in the lubricant structure affects the level of their anti-wear properties, as evidenced by the results obtained during the tribological tests presented in this article. The highest resistance to wear was noted for lubricants containing 3% of modifying additive, which was reflected in the results of the LLW parameter test.

The tests conducted have shown that the introduction of a modifying additive to the lubricating compositions significantly changes the internal structure of the tested lubricants. The reason for this is the chemical structure of the additive used.

The obtained results of the flow curves allow for the conclusion, that the rheological properties (yield point) of the tested lubricant compositions changed significantly depending on the amount of used modifying additive. Modifying the vegetable lubricants with titanium dioxide reduces their yield point. The magnitude of changes of the yield point value depends on the chemical structure and physicochemical properties of the base oil, shaped by intermolecular interactions - mainly van der Waals forces, and the amount of the modifying additive.

The introduction of increasing amounts of modifier into the grease caused an decreased of dynamic viscosity at lower temperature values. The introduction of 3 % of titanium dioxide into the lubricating composition revealed a significant increase of dynamic viscosity at higher temperature in compared to the basic grease. Assessing changes of dynamic viscosity in temperature for the tested lubricating compositions it should be noted, that the introduction of titanium dioxide into the structure of greases caused a minimum changes of viscosity in wide range of temperature.

The introduction of increasing amounts of modifier into the grease caused a significant changes of dynamic viscosity at lower shear rate values. The value of dynamic viscosity of the tested lubricating compositions decreased along with the increasing amount of additive in lower values of shear rate.

All the tested vegetable lubricants modified with titanium dioxide in different degree showed the phenomenon of thixotropy, visible as the lack of overlapping of the flow curves obtained at increasing and decreasing shear rates.

The highest value of the thixotropy hysteresis surface area was observed in vegetable lubricant modified with 3% of titanium dioxide, while the lowest value was observed in the modified lubricant with 5% of used additive. The most effective action of the additive was observed for composition D, which restored the damaged structure most quickly.

The results of the study of influence of modifying additive for vegetable lubricating greases were allowed to the conclude, that:

- the change of the lubricating durability of tested lubricating greases it depends from the chemical structure of the dispersed phase, dispersion phase and used additive and also the interactions between the components creating 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 anti-wear properties of tested lubricating greases,
- the analysis of the results of tribological 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 thickener and additive but also oxidation products and tribochemical reaction products with the friction pair working surface. The activity of the used additive 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,
- the change of dynamic viscosity for the lubricating composition caused the change of friction factor and change the anti-wear protection of tribosystem lubricated of tested lubricating greases,
- the appearance of oxidation products can be explained by the good antiwear properties of greases, determined by the diameter of the scar of wear,
- the analysis of the results of tribological tests connected with the analysis of the change the structure of the grease after tribological tests allows to state, that lubricating properties are not only a derivative of the amount of additive, but also the oxidation products, which protect the tribosystem,
- the magnitude of changes of the yield point value depends on the chemical structure and physicochemical properties of the base oil, shaped by intermolecular interactions - mainly van der Waals forces, and the amount of the modifying additive,
- an increasing quantity of titanium dioxide into the grease caused an decreased of dynamic viscosity at lower temperature values and a significant changes of dynamic viscosity at lower shear rate values,
- lubricants modified with titanium dioxide changed the rate of thixotropy and efficiency of reconstruction structure in short time.

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