Nafta-Gaz 2020, no. 4, pp. 270–278, DOI: 10.18668/NG.2020.04.06

The influence of montmorillonite content on change the physicochemical properties of lubricating greases produced from vegetable base oil

Wpływ zawartości montmorylonitu na zmianę właściwości fizykochemicznych smarów plastycznych wytworzonych na bazie roślinnej

Rafał Kozdrach

Research Network Łukasiewicz – Institute for Sustainable Technologies

ABSTRACT: The publication presents the results of investigations into the influence of different amounts of a modifying additive on the physicochemical properties of selected lubricating compositions. Montmorillonite, as a representative of stratified silicates, was used to modify lubricating grease produced from a vegetable base oil, and lithium stearate was used to thicken it. Investigations of the physicochemical properties of the base lubricating grease were carried out and compared with the results obtained for lubricating greases containing the modifying additive. The selected parameters were penetration, penetration after prolonged kneading, dropping point, emission of oil from grease, anticorrosive properties by dynamic method, and mechanical stability – an attempt to roll out and oxidize the lubricant with a PetroOxy apparatus. Based on the results of physicochemical tests, it was determined that the applied modifying additive causes an increase in the dropping point, which limits the applicability of lubricating greases, as well as a decrease in oil emission, which was responsible for the lubricating effectiveness of the tested lubricants. It had a positive effect on mechanical stability and the tested lubricants were not disqualified from use in established applications, reducing the degree of corrosion on ball bearings working in the presence of the lubricating greases during testing. This had a positive effect on the condition of machines and devices where the lubricating greases are used and increased the oxidative stability when its content in the lubricating grease was at least 5%. This figure represents the upper limit of the modifying additive content in the lubricating greases.

Key words: lubricating grease, modifying additive, stratified silicate, physicochemical properties, penetration, penetration after prolonged kneading, dropping point, emission of oil, anti-corrosive properties by dynamic method, mechanical stability, oxidation.

STRESZCZENIE: W publikacji przedstawiono wyniki badań wpływu różnej ilości dodatku modyfikującego na właściwości fizykochemiczne wybranych kompozycji smarowych. Do modyfikacji smaru plastycznego wytworzonego na bazie roślinnej i zagęszczonego stearynianem litu zastosowano montmorylonit, przedstawiciela krzemianów warstwowych. Wykonano badania właściwości fizykochemicznych smaru plastycznego bazowego oraz smarów plastycznych zawierających dodatek modyfikujący, a otrzymane wyniki porównano. Wyznaczono penetrację, penetrację po przedłużonym ugniataniu, temperaturę kroplenia, wydzielanie oleju ze smaru, właściwości przeciwkorozyjne uzyskane metodą dynamiczną, stabilność mechaniczną – próba wałkowania oraz utlenialność na aparacie PetroOxy. Na podstawie analizy otrzymanych wyników badań fizykochemicznych stwierdzono, że zastosowany dodatek modyfikujący powoduje wzrost temperatury kroplenia, która decyduje o granicy stosowalności wytworzonych smarów plastycznych oraz wpływa na spadek wydzielania oleju ze smaru, który świadczy o skuteczności smarowania elementów trących badanymi kompozycjami smarowymi. Dodatek wpływa korzystnie na stabilność mechaniczną, zmniejsza stopień skorodowania łożysk kulkowych pracujących w obecności badanych smarów plastycznych, co z kolei korzystnie oddziałuje na stan maszyn i urządzeń, w których smary te są stosowane, oraz zwiększa stabilność oksydacyjną, gdy zawartość dodatku w smarze wynosi co najmniej 5%.

Słowa kluczowe: smar plastyczny, dodatek modyfikujący, krzemian warstwowy, właściwości fizykochemiczne, penetracja, penetracja po przedłużonym ugniataniu, temperatura kroplenia, wydzielanie oleju, właściwości przeciwkorozyjne oznaczone metodą dynamiczną, stabilność mechaniczna, utlenialność.

Corresponding author: R. Kozdrach, e-mail: *rafal.kozdrach@itee.radom.pl*

Article contributed to the Editor: 05.11.2019. Approved for publication: 26.03.2020

Introduction

The properties of lubricating greases depend on their composition and manufacturing technology, and are shaped by means of respectively selected ennobling additives (Mortier et al., 2010). Typical packages contain antioxidants (to increase the resistance to oxidation), antiwear and antiscuffing additives (to improve the tribological properties of the product), anticorrosive additives (to reduce the aggressiveness of the lubricating grease in comparison to metals), adhesives (to improve the adhesiveness to the construction elements of machines), and rheological additives. Not only does the presence of additives determine the utility properties of a lubricating grease, but so does the method of incorporating them into the structure of the grease. The insertion of additives into lubricating greases can cause many technological difficulties because a molecule of additive is adsorbed onto the surface of the thickener, which may consequently carry on to reduce the effectiveness of the component, and even reduce the stability of the lubricating grease (Czarny, 2004; Donahue, 2006; Rizvi, 2009; Rudnick, 2009; Mortier et al., 2010; Brown, 2015).

Highly refined, high-purity rapeseed oil was used as the dispersing phase. Refined rapeseed oil does not contain free acids or any organic suspensions; it is yellow-brown in color and odorless, and it has a viscosity of 68 mm^2/s at 20°C, a pour point of –17°C, a flash point of 292°C, and a density of 878 kg/m^3 at 15°C. This oil is used as a raw material in the production of biofuels and as a component in the production of animal feed, cleaning agents, paints, varnishes, adhesives, and asphalt emulsions. It is used in the food, cosmetics, and pharmaceutical industries, as an additive in the production of plastic masses, as an ingredient in the production of floor coverings, as a lubricant that protects food machinery parts against wear and seizure, and as an oil base for plastic lubricants (Kobylarz, 1997).

Lithium 12-hydrostearate, which is a white solid in the form of a powder, was used as the dispersed phase of the tested lubricating compositions. It has a high melting point of 200°C, so it can be used as a dispersed phase in plastic greases. Today, most lubricants used in motor vehicles, aircraft, and heavy machinery contain lithium stearates, mainly lithium 12-hydroxystearate (Wietelmann and Bauer, 2000). Lubricants can be obtained with the addition of several different metallic soaps. Some lubricants are made from lithium hydroxide, sodium, barium, and calcium soaps. Lithium-soap-based lubricants are often used because of their high water resistance and mechanical stability and low oxidation. Soap thickeners also have good properties at high or low temperatures, depending on the type of fatty acid. To obtain lithium 12-hydroxystearate, lithium hydroxide and fatty acid are combined in an aqueous medium. During vigorous stirring, diluted lithium hydroxide monohydrate is gradually added to a suspension of fatty acid in water heated to just below its boiling point (Nora et al., 2005). The content of 12-hydroxystearic acid in the resulting salt is 96–98%. Lithium 12-hydroxystearate is typically used in synthetic oils, such as silicone or ester oils, but this does not exclude its use in mineral or vegetable oils. Synthetic oils are more beneficial because of their greater stability and ability to work at extreme temperatures. 12-hydroxystearic acid is obtained by hydrogenating castor oil (Maskaev et al., 1971). After the primary double bond saturation reaction, dehydration and reduction of the hydroxyl group are carried out with stearic acid.

Because lubricating greases should be used opportunely, specially selected additives to improve their utility properties. The lubricating greases are mixed 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 chemical resistance and better resistance to high temperatures. Generally, for this type of additive, graphite, molybdenum disulfide, polytetrafluoroethylene, copper and chloroparaffins are used (Rizvi, 2009; Lugt, 2009).

The current study owes its innovation to nanotechnology, which denotes a structure with at least one dimension measuring less than 100 nm (Mazurkiewicz et al., 2006). The introduction of nanoadditives to the structure of lubricating grease causes a pronounced improvement in the antiscuffing and antiwear properties, as well as improving the rheological properties from which depend on the utility properties of lubricating compositions (Kozdrach and Molenda, 2012; Kozdrach, 2012a, 2015a). These characteristics explain the large interest in innovative nanoadditives. The negative aspects of using nanoadditives is their high cost and limited availability and the difficulties in achieving the required degree of dispersion throughout the structure of the lubricating grease. A proportion of 1–7% nanoadditives introduced into the lubricating compositions was sufficient for the specific, high requirements for lubricating greases (Bhattacharyya and Gupta, 2008; Kozdrach et al., 2010).

Stratified nanosilicates play an especially important role. Usually, montmorillonite is used with a formula $M_x(Al_4\text{-}xMg_x)Si_8O_{20}(OH)_4$ and a particle size of 100–150 nm. They are constructed of three-layer packages, containing one octahedral layer situated between two tetrahedral layers (Fig. 1) (Sinha Ray and Okamoto, 2003; Kacperski, 2003; Bhattacharyya and Gupta, 2008; Kozdrach et al., 2010). The octahedral layer is made of aluminum or magnesium oxide and is connected to the two outer layers of silicon (tetrahedral) through their common oxygen atoms. Modified by means of a quaternary ammonium salt, it becomes hydrophobic and organophilic, which allows for the absorption of the same quantity of organic liquids, e.g., oils.

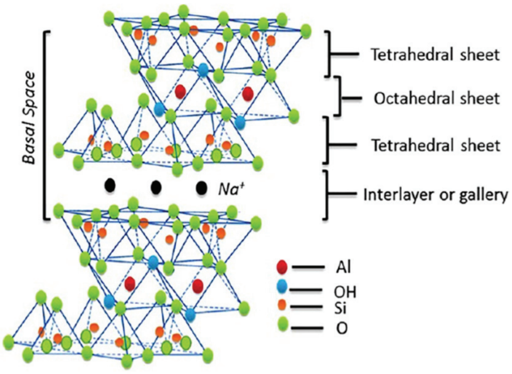

Fig. 1. The chemical structure of montmorillonite (Bhattacharyya and Gupta, 2008)

Rys. 1. Struktura chemiczna montmorylonitu (Bhattacharyya and Gupta, 2008)

The modified montmorillonite is compatible with lubricating greases and is used to modify the rheological and lubricating properties (Giannelis et al., 1999; Królikowski and Rosłaniec, 2004; Piecyk, 2006; Pagacz and Pielichowski, 2007; Kozdrach, 2017). An organic hydrophobic medium is chemically connected to the surface of the montmorillonite, which allows the montmorillonite and lubricating greases to be permanently connected. Additionally, as a result of replacing the cations, the distance between the layers is increased from approximately 1 nm for natural montmorillonite to 2–3 nm in the case of the modified organic compounds (Piecyk, 2006; Pagacz and Pielichowski, 2007; Mencel et al., 2009; Kozdrach, 2017, 2018).

The physicochemical properties of the additive used are presented in Table 1.

Table 1. The physicochemical properties of the modifying additive

Tabela 1. Właściwości fizykochemiczne dodatku modyfikującego

Physicochemical properties of the additive, montmorillonite (data from the safety data sheet)			
Density	2.24 g/cm³	Moisture content	5.5%
Moh's hardness	1.36 [-]	Melting point	> 1300°C
Shine	matte	Compressive strength	7.5 RcwN/cm²
Clarity	transparent	pH	9.1 [-]
Color	white	Temperature of self-ignition	190°C
Cleavage	excellent	Volatile matter content	0.06%
Surface	irregular	Flash point	185°C
Refractive index	1.518 [-]	Boiling point	378°C
Molar mass	549.07 g/mol	Chemical content:	
		O	64.11%
		Na	0.84%
		Ca	0.73%
		Al	9.83%
		Si	20.46%
		H	4.04%

The aim of the study was to examine the influence of different amounts of montmorillonite, as a modifying additive, on the basic physicochemical parameters of lubricating compositions used in the food industry; the study was conducted at the Łukasiewicz Research Network – the Institute of Sustainable Technologies in Radom.

Experimental part

The characteristics of the test materials

The lubricating grease used in the test was based on a vegetable base oil (Kozdrach, 2016a, 2016b; Drabik et al., 2018a, 2018b, 2018c; Iłowska et al., 2018; Kozdrach and Skowroński, 2018a, 2018b; Szmatoła et al. 2018). Lithium stearate was used as a thickener for the lubricating grease. This lubricating composition was then modified by various amounts of modified stratified silicate in the form of montmorillonite. An additive, in the amounts of 1%, 3%, and 5% m/m of each lubricating grease was introduced to the structure. The lubricating compositions were subsequently labelled with the following symbols: A (basic lubricating grease), B (lubricating grease with 1% montmorillonite), C (lubricating grease with 3% montmorillonite), and D (lubricating grease with 5% montmorillonite). In the early phase of the experiment, research was done to arrive at the above amounts of additive to be introduced into the lubricating composition. Tests were carried out with compositions containing from 1% to 10% of modifying additive.

The lubricating greases thus produced were tested for their physicochemical properties, and the results obtained were compared with the results for the base lubricating grease (Ischuk and Umanskaya, 1994; Pogosyan and Martirosyan, 2008; Chengfei et al., 2016; Cao et al., 2017; Razak et al., 2019).

Using standardized tests, dropping point, penetration, penetration after prolonged kneading, emission of oil from grease, anticorrosive properties by dynamic method, and mechanical stability – an attempt to roll out and oxidize with a PetroOxy apparatus – were all determined for the lubricating compositions.

The methodology of research

The dropping point measurement was carried out according to the norm PN-ISO 2176:2011. The rule of determination consisted of determining the temperature at which the first drop of lubricating grease flows from the test dishes under uniform heating. The arithmetic average of measurements from two thermometers was used: one in the test tube with the tested grease and one in the oil bath (Kozdrach et al., 2010).

The penetration test was carried out according to PN-ISO 2137:2011. The method of determination consisted in measuring the depth of gravitational dipping, standardized cone in tested lubricating grease at a temperature of 25°C, dropping within 5 s. The penetration was expressed in "penetration units" (unit less number responsible to 0.1 mm the immersion of cone in the grease being tested). The resulting measurement was accepted if the arithmetic average of three measurements did not differ by more than one penetration unit. In order to determine the penetration after prolonged kneading, the lubricating grease was subjected to mechanical kneading using 10,000 cycles. The measurement of penetration was carried out immediately after the kneading process. The difference between this penetration and the initial penetration (60 cycles) was defined as the mechanical resistance of lubricating grease and is given as a percentage (Molenda et al., 2001, 2003; Bajer and Janecki, 2004; Bajer, 2007; Kozdrach et al., 2010).

The test of emission of oil from the lubricating greases was carried out according to PN-V-04047:2002. The method of determination consists in measuring, under static conditions, the quantity of oil which separates from a lubricating grease, located in a nickel cone at 100°C, within 30 hours. The quantity of separated oil is given as a mass fraction in percent (Kozdrach et al., 2010).

The test of thermos-oxidative stability was carried out with a PetroOxy apparatus. A sample with 5 ml of the grease was introduced into the test chamber of the device and was subjected to oxidation with oxygen at a constant temperature of 120°C. The filling pressure was 700 kPa, and the oxygen pressure was 8 bar (800 kPa). The time needed to obtain a maximum decrease of pressure in the measuring chamber by about 10% was used as the result (Molenda et al., 2010).

The investigation of anticorrosion properties of lubricating greases by the dynamic method was carried out according to PN-79/C-04175. The method consists in adding 10 g of the lubricating grease to at least two oscillatory ball bearings installed on a horizontal roller and situated in split mounts; 20 cm^3 of distilled water is added to each mount. The test was carried out at a temperature of 18–28°C. The test position was run for 8 h and then allowed for 16 h. A cycle of 8 h working and 16 h stopping was repeated; then the test position was run for 8 h and then allowed to stand for 108 h. After removing the mounts, the roller with bearings was removed and the bearings were evaluated for the degree of corrosion. The results are given in percent of corroded surface or determined the degree of corrosion in points.

The test of the mechanical stability of the lubricating greases, called the rolling test, was carried out according to PN-62/C-04144. The test consists in determining the penetration of a lubricating grease after 60 cycles, then filling a cylinder with 75–80 g of lubricating grease before kneading in a dish penetration. The cylinder is placed into the apparatus for rolling and the test carried out at 60°C at a speed of 165 rpm for 4 h. The lubricating grease is then removed from the cylinder and cooled to 25°C. The cooled lubricating grease is moved into the penetration dish and its penetration is marked. The increase in penetration is calculated in percent.

The results of physicochemical research of lubricating greases

A comparison of the results of tests on the influence of the modifying additive on the dropping point for the lubricating compositions are presented in Fig. 2.

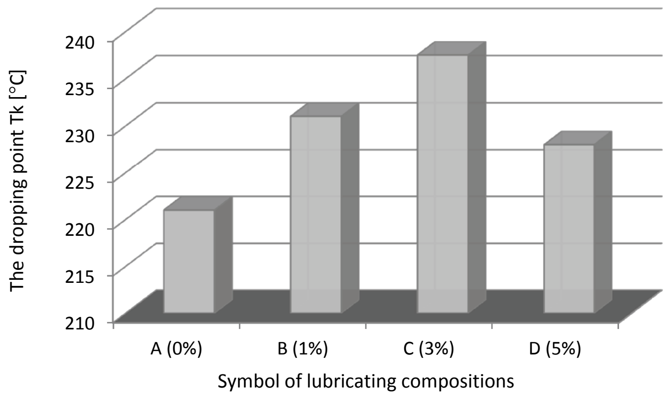

Fig. 2. The influence of different quantities of modifying additive on the change in dropping point of lubricating greases

Rys. 2. Wpływ różnej ilości dodatku modyfikującego na zmianę temperatury kroplenia badanych smarów plastycznych

In each case, the introduction of the modifying additive, i.e., montmorillonite, to the structure of the lubricating grease caused an increase in dropping point relative to the dropping point of the basic lubricating grease, i.e., without the modifying additive. This increase was 4.5% in the case of lubricating grease modified with 1% montmorillonite, 6.8% in the case of lubricating grease modified with 3% modifying additive, and 3.2% in the case of lubricating grease with 5% montmorillonite.

Based on the analysis of the testes carried out, it was ascertained that the introduction of 1–5% of montmorillonite into the structure of lubricating grease caused an increase in the dropping point of lubricating greases in comparison to the starting composition, which indicated an improvement in the structural stability of the tested lubricants (Fig. 2). However, the best effect of the modifying additive was provided to the composition which contained 3% of the modifier in its structure, because the highest value of this parameter was obtained for this composition.

It can be concluded that the changes of the dropping point of the tested lubricating greases were addicted on the amount of modifying additive used. The addition of 3% modifying additive to the lubricating greases caused an increase in the chemical stability of the lubricating compositions.

The application area of lubricating greases depends (among other things) on the consistency class. This formed the basis for evaluating the rheological properties of lubricating greases. The results of this parameter obtained through testing are presented in Fig. 3.

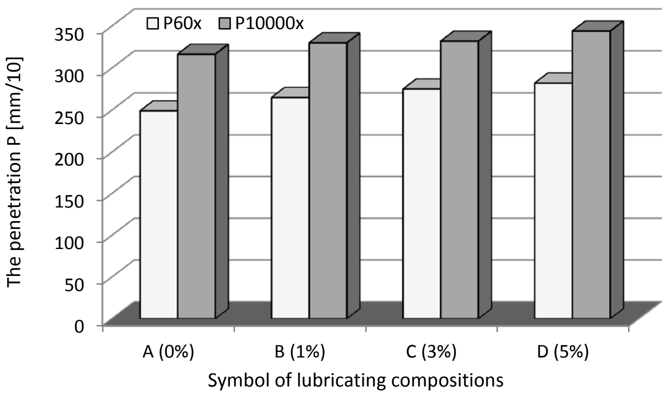

Fig. 3. The influence of different quantities of the modifying additive and mechanical extortion on the penetration in the lubricating greases under study

Rys. 3. Wpływ różnej ilości dodatku modyfikującego i wymuszeń mechanicznych na zmianę penetracji badanych smarów plastycznych

It was ascertained that the modifying additive caused favorable changes in the penetration of the tested lubricating compositions, because in each case an increase in this parameter was found in comparison to the value resulting of change the consistency class. The lubricating composition without the modifier belonged to the 3rd class of consistency (penetration range: 220–250 mm/10), and the compositions modified with montmorillonite were in the 2nd class of consistency (penetration range: 265–295 mm/10). It follows that the changes in penetration showed on change of the mechanical stability of the tested lubricating compositions. Thus, the introduction of different amounts of montmorillonite into the greases' structure did not positively affect the mechanical stability of the tested greases. The greatest change was observed for composition D, which was modified with 5% montmorillonite (the increase in penetration was approximately 13.2%), in comparison to composition A, which did not contain any modifying additive, while the smallest change was observed for composition B, which was modified with 1% montmorillonite (the increase in penetration was approximately 6.4%), in comparison with composition A containing no modifying additive.

The changes in penetration after prolonged kneading were also evaluated (Fig. 3). In this case, the largest change was observed for composition D, which was modified with 5% montmorillonite (the increase in penetration was approximately 8.7%), in comparison with the composition which did not contain any modifying additive, whereas the least change was observed for composition B, to whose structure was added 1% of the modifier (the increase in penetration was approximately 4.3% in relative to the grease deprived of modifying additive). The changes in penetration indicated a change in the mechanical stability. In all cases, the mechanical stability of the greases were improved. It can be concluded that introducing the modifier to the structure of the lubricating greases tested has a favorable effect on their mechanical stability.

The increase in penetration of the tested lubricating compositions induced the presence of different amounts of modifier and the mechanical kneading process did not cause a significant change in their utility or physicochemical properties. Based on the results of the tests, it can be concluded that a slight increase in penetration (on the order of several percentage points) does not disqualify the tested lubricating greases from established applications. In the chemical industry – including the food industry – there are applications for lubricants with different consistencies (in a wide range of penetration values), so the application of received lubricating greases was most reasonable particular, that they did not lose their lubricating properties (Kozdrach et al., 2010; Kozdrach, 2012a, 2012b, 2015a; 2015b, 2016c). The norm PN-ISO 2137:2011, on the measurement of the penetration of lubricating greases, allows for a change in penetration after prolonged kneading to 40 units of penetration.

For selected lubricating compositions, tests of the emission of oil were carried out. The influence of different amounts of the modifying additive on oil emission from the greases are presented in Fig. 4.

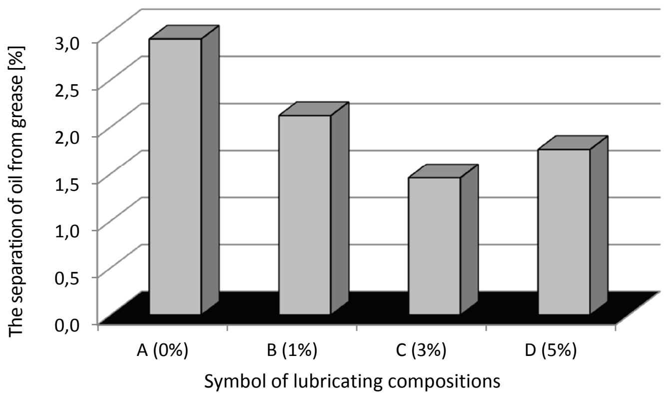

Fig. 4. The influence of different quantities of modifying additive on the change in oil separation from lubricating greases

Rys. 4. Wpływ różnej ilości dodatku modyfikującego na zmianę parametru wydzielania oleju ze smaru dla badanych smarów plastycznych

The test of oil emission from the greases revealed and a tendency for the oil to separate during storage. It was observed that composition C has the most stable structure, which was modified with 3% montmorillonite, and that composition A was the least stable, which did not contain any modifying additive. The different amounts of modifying additive introduced into the base lubricating grease caused an increase in the structural stability of the lubricating greases in every case, as seen by the lower amount of separated oil in the tested lubricating greases in comparison with the unmodified grease.

It should be noted that norm PN-72/C-96134, on the emission of oil from bearing greases, LT specifies that the amount of separated oil from lubricating greases without losing their lubricating ability should not exceed 10%. The introduction of different amounts of montmorillonite as a modifying additive to the structure of the tested lubricating greases clearly reduces the amount of isolated oil from the grease in comparison with the basic, unmodified lubricating grease, in all cases.

The introduction of different amounts of modifying additive to the tested lubricating greases caused a reduction in the amount of separated oil, which in turn has a positive effect on the phenomenon of syneresis (the release of the dispersing agent from the gel), which affects the efficiency of lubrication. In order to not lose its lubricating properties, each grease should emit an equable, slight amount of oil, which provides a film of the required thickness between the lubricated surfaces.

Tests of the anticorrosive properties of the selected lubricating compositions were carried out by the dynamic method, as well as tests of mechanical stability (the rolling test). The influence of different amounts of modifying additive on the anticorrosion properties are presented in Fig. 5, and of the mechanical stability of the greases are presented in Fig. 6.

The tests of the anticorrosion properties of lubricating greases by the dynamic method were carried out according to norm PN-79/C-04175. This method allows researchers to determine the degree of corrosion on ball bearings which are working in the presence of greases under extreme conditions. It was ascertained that the most favorable anticorrosion properties were demonstrated by composition C, which was modified with 3% modifying additive (only 1% of the surface of the bearings were corroded), while composition A, which did not have any additive in its composition, was characterized by the weakest properties of corrosion (4% of the surface of the bearings were corroded).

It should be noted that PN-79/C-04175 does not specify the maximum degree of acceptable corrosion on ball bearings which are working in the presence of lubricating grease without losing its functional abilities. The introduction of different amounts of montmorillonite as a modifying additive to the structure of the tested greases in each case reduced the degree of corrosion of the ball bearings working in the presence of those lubricating greases in comparison with the base grease, which was not modified with the modifying additive.

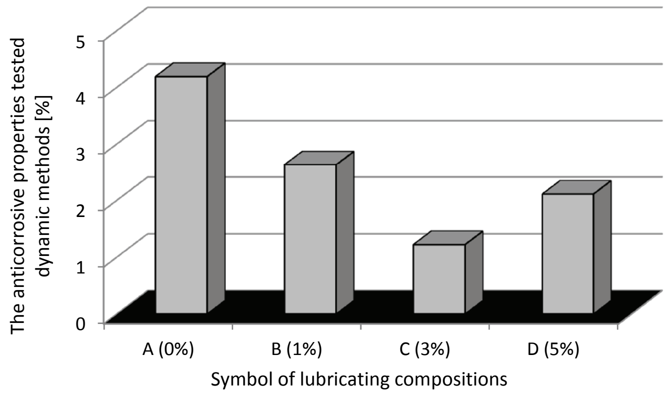

Fig. 5. The influence of different quantities of modifying additive on the change in the anticorrosive properties of lubricating greases, tested by the dynamic method

Rys. 5. Wpływ różnej ilości dodatku modyfikującego na zmianę właściwości antykorozyjnych wyznaczonych metodą dynamiczną dla badanych smarów plastycznych

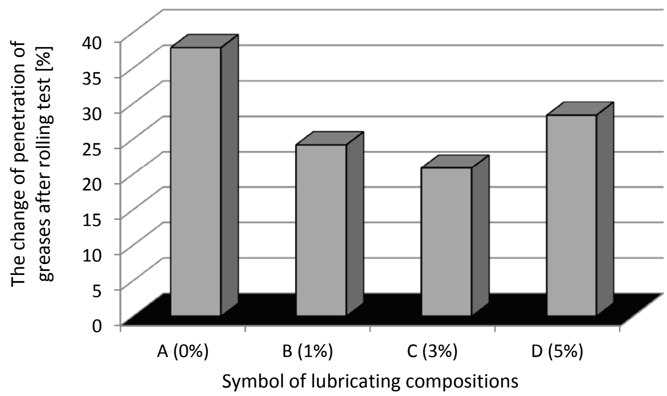

Fig. 6. The influence of different quantities of modifying additive on the change in the penetration of lubricating greases after the rolling test

Rys. 6. Wpływ różnej ilości dodatku modyfikującego na zmianę penetracji smarów po teście wałkowania dla badanych smarów plastycznych

The introduction of different amounts of modifying additive to the tested lubricating greases caused a reduction in the corrosion of the ball bearings, which in turn would have a positive effect on the condition of machines and devices where the greases are used.

The study of the mechanical stability of greases, called the rolling test, was carried out according to PN-62/C-04144. This method allows researchers to determine the change in penetration to tested lubricating greases which are working under extreme conditions. It should be noted that PN-62/C-04144 does not specify the maximum change in mechanical stability, expressed by the difference in micropenetration (in percent) before and after the rolling test without losing the functional abilities of the grease.

It was determined that the modifying additive has a positive effect on micropenetration after the rolling test for the tested lubricating compositions, because in each case the percentage change of micropenetration was lower than the change of micropenetration for the base lubricating grease without any modifying additive. The largest change in mechanical stability was observed for composition A, which did not contain any modifier (the change in micropenetration before and after the rolling test was 37.9%), while the least change in mechanical stability was observed for composition C, which was modified with 3% montmorillonite (the change in micropenetration before and after the rolling test was 20.9%).

In all cases, the mechanical stability of greases modified with montmorillonite was improved in comparison to that of the base lubricating grease without any modifying additive. It can be concluded that introducing a modifier to the structure of lubricating greases has a positive effect on the mechanical stability of said greases.

The change in micropenetration of the tested lubricating compositions after the rolling test caused by the presence of different amounts of modifier does not cause a significant change in their useful properties. Based on the results of the research, it can be concluded that the change in mechanical stability (even up to several percentage points) will not disqualify the tested greases from their intended applications, so the use of the lubricating greases is most justified, especially because the level of their lubricating properties does not change (Kozdrach et al., 2010; Kozdrach, 2012a, 2012b, 2015a, 2015b, 2016c).

For the selected lubricating compositions, the oxidation test was carried out using a PetroOxy apparatus. The influence of various amounts of the modifying additive on the oxidation of lubricating greases is presented in Fig. 7.

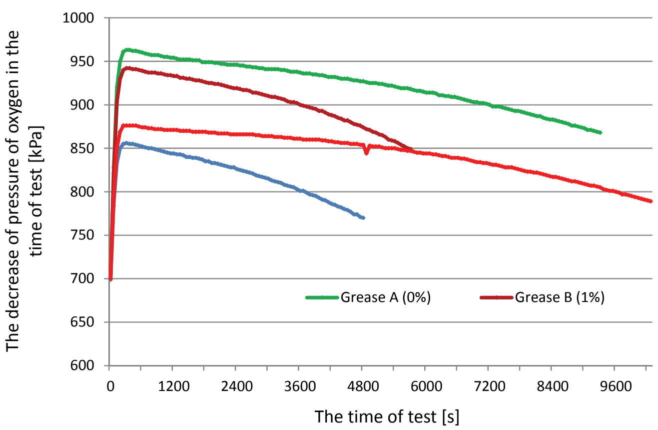

Fig. 7. The influence of different quantities of modifying additive on the change in oxidation stability of lubricating greases

Rys. 7. Wpływ różnej ilości dodatku modyfikującego na zmianę stabilności oksydacyjnej dla badanych smarów plastycznych

The test of the oxidation of the lubricating compositions carried out using a PetroOxy apparatus at a temperature of 120°C consisted in determining the influence the amount of modifying additive introduced into the lubricating greases exerted on the results of the measurements. It was observed that the induction period of oxidation for the tested lubricating compositions differed significantly from each other. No linear dependence between increasing content of the modifying additive in the lubricating grease and the time of induction of oxidation was observed. The lubricating compositions modified with 1–3% of montmorillonite were characterized by a significantly shorter induction period of oxidation than the base composition without any modifying additive, while the lubricating grease modified with 5% of the additive extended the time of induction by about 7%. Thus, the results clearly indicate that the introduction of 1%–3% of the modifying additive reduced the oxidative stability, and that the introduction of 5% of the modifier to the tested lubricating compositions caused an increase in oxidation stability.

Summary

Based on the results, it may be concluded that the physicochemical properties of the tested lubricating compositions were significantly different according to the content of the modifying additive within them.

The modifier used in these tests was an effective additive for improving the physicochemical properties of the tested lubricating greases. Its inclusion in the structure of the grease provided an increase in dropping point, which determines the limit of the product's applicability, and a decrease in oil emission from the grease, which was is responsible for the lubricating effect of lubricating compositions.

The modification of the tested lubricating compositions with various amounts of montmorillonite caused an increase in penetration, though it did not cause any essential change in their utility. In all cases, the mechanical stability of the greases were improved. It can be concluded that introducing this modifier to the structure of greases has a favorable effect on mechanical stability and does not disqualify the tested lubricating compositions from their established applications.

The introduction of different amounts of montmorillonite as a modifying additive to the structure of the tested greases decreased the degree of corrosion of the ball bearings working in the presence of the lubricating greases in each case in comparison with the base grease, which was not modified with an applied additive, which in turn will have a beneficial effect on the condition of any machines and devices where the greases are to be used.

The change in micropenetration of the tested lubricating compositions after the rolling test caused by various amounts of the modifier was favorable, as in each case the percentage change of micropenetration was lower than that of the base lubricating grease without any modifying additive.

The lubricating compositions modified with 1–3% of montmorillonite displayed a significantly shorter time of induction of oxidation – as determined by the PetroOxy test – than the base composition without any modifying additive, as resulting of reduction of oxidative stability. However, the lubricating grease modified with 5% additive was characterized by a longer induction time of oxidation of about 7%, so its oxidative stability increased.

References

Bajer J., 2007. Wpływ wymuszeń mechanicznych i wody na charakterystyki tribologiczne smaru plastycznego. *Tribologia,* 6: 63–73.

Bajer J., Janecki J., 2004. Syntetyczne smary plastyczne do różnych zastosowań. *Problemy Eksploatacji*, 2: 199–206.

Bhattacharyya K.G., Gupta S.S., 2008. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. *Adv. Colloid Interface Sci.*, 140: 114–131.

Brown S. F., 2015. Additives for lubricating grease. *Tribology & Lubrication Technology,* **12:** 18–22.

Cao Z., Xia Y., Xi X., 2017. Nano-montmorillonite- doped lubricating grease exhibiting excellent insulating and tribological properties. *Friction,* 5(2): 219–230. DOI 10.1007/s40544-017-0152-z.

Chengfei S., Xiaochuan G., Mingjun J., Yan H., 2016. Study on the Effect of Surface Modification on the Properties of Bentonite Greases. *China Petroleum Processing and Petrochemical Technology*, 18(4): 99–109.

Czarny R., 2004. Smary plastyczne. *WNT, Warszawa*.

Donahue C.J., 2006. Lubricating Grease: A Chemical Primer. *Journal of chemical Education,* 6: 862–865.DOI:10.1021/ed083p862.

Drabik J., Kozdrach R., Wolszczak M., Wrona M., 2018a. The pro-ecological base oils of highly specialized lubricants. *Przemysł Chemiczny,* 9: 538–541. DOI: 10.15199/62.2018.9.30.

Drabik J., Trzos M., Kozdrach R., Wrona M., Wolszczak M., Duszyński G., Piątkowski M., 2018c. Modeling and evaluation of properties of lubricants used in the food industry. *Przemysł Chemiczny,* 12: 2200–2204. DOI: 10.15199/62.2018.12.39.

Drabik J., Trzos M., Pawelec E., Wrona M., Kozdrach R., Duszyński G., Piątkowski M., 2018b. Badanie właściwości użytkowych ekologicznych smarów wytworzonych na olejowych bazach roślinnych. *Przemysł Chemiczny*,12: 2194–2199. DOI: 10.15199/62.2018.12.38.

Giannelis E.P., Krishnamoor R., Manias E., 1999. Polymer silica nanocomposites: model systems for confined polymers and polymers brushes. *Advance Polymer Science,* 118: 108–122. DOI: 10.1007/3-540-69711-X_3.

Iłowska J., Chrobak J., Grabowski R., Szmatoła M., Woch J., Szwach I., Drabik J., Trzos M., Kozdrach R., Wrona M., 2018. Designing Lubricating Properties of Vegetable Base Oils. *Molecules, 23:* 2025-2035. DOI: 10.3390/molecules23082025.

Ischuk Y.L., Umanskaya O.I., 1994. Modified montmorillonite clays used in the manufacture of lubricating greases. *NLGI Spokesman*, 58(7): 9–11.

Kacperski M., 2003. Nanokompozyty polimerowe. Cz. II. Nanokompozyty na podstawie polimerów termoplastycznych i krzemianów warstwowych. *Polimery,* 2: 83–90.

Kobylarz J., 1997. Oleje smarowe i hydrauliczne uzyskane na bazie oleju rzepakowego. *Przegląd Techniki Rolniczej i Leśnej*, 3: 10–16.

Kozdrach R., 2012a. Wpływ nanododatków ceramicznych na charakterystyki tribologiczne biodegradowalnych smarów plastycznych. *Tribologia*, 4: 75–88.

Kozdrach R., 2012b. Wpływ wymuszeń mechanicznych na zmianę właściwości smarnych biodegradowalnego smaru plastycznego wytworzonego na bazie roślinnej. *Nafta-Gaz,* 11: 868–876.

Kozdrach R., 2015a. Wpływ synergizmu dodatków zawierających krzem na zmiany charakterystyk trybologicznych smaru plastycznego. *Nafta-Gaz*, 2: 110–118.

Kozdrach R., 2015b. Zastosowanie montmorylonitu jako dodatku modyfikującego właściwości tribologiczne smaru plastycznego wytworzonego na bazie roślinnej. *Nafta-Gaz,* 12: 1029–1036. DOI: 10.18668/NG2015.12.12.

Kozdrach R., 2016a. The influence of different vegetable dispersion phase on rolling contact fatigue of biodegradable lubricating greases. *Tribologia,* 6: 57–67. DOI: 10.5604/01.3001.0010.6716.

Kozdrach R., 2016b. The tribological properties of lubricating greases based on renewable oils. *Tribologia*, 2: 61–72. DOI: 10.5604/01.3001.0010.7565.

Kozdrach R., 2016c. Wpływ wymuszeń mechanicznych na zmianę właściwości tribologicznych smarów plastycznych wytworzonych na bazie mineralnej. *Nafta-Gaz,* 1: 50–57. DOI: 10.18668/NG2016.01.07**.**

Kozdrach R., 2017. Wpływ montmorylonitu na wartość granicy płynięcia smaru plastycznego wytworzonego na bazie roślinnej. *Nafta-Gaz*, 9: 698–706. DOI: 10.18668/NG.2017.09.10.

Kozdrach R., 2018. Wpływ rodzaju fazy zdyspergowanej na właściwości tribologiczne smarów plastycznych wytworzonych na oleju lnianym. *Nafta-Gaz*, 6: 471–478. DOI: 10.18668/NG.2018.06.08.

Kozdrach R., Drabik J., Pawelec E., Molenda J., 2010. Wpływ dodatku modyfikującego na bazie polimerowo-krzemionkowej oraz wymuszeń mechanicznych na właściwości fizykochemiczne ekologicznych smarów plastycznych. *Tribologia*, 2: 35–46.

Kozdrach R., Molenda J., 2012. Testowanie właściwości eksploatacyjnych ekologicznych smarów plastycznych modyfikowanych dodatkiem polimerowo-krzemionkowym. *Tribologia*, 6: 99–111.

Kozdrach R., Skowroński J., 2018a. The application of chitosan as a modifier for lubricating greases based on vegetable oil. *Tribology in Industry*, 2: 212–219, DOI: 10.24874/ti.2019.41.02.07.

Kozdrach R., Skowroński J., 2018b. The application of polyvinylopirrolidone as a modifier of tribological properties of lubricating greases based on linseed oil. *Journal of Tribology*, 140(6): 1801–1807. DOI: 10.1115/1.4040054.

Królikowski W., Rosłaniec Z., 2004. Nanokompozyty polimerowe. *Kompozyty,* 4: 3–16.

Lugt P.M., 2009. A Review on Grease Lubrication in Rolling Bearings. *Tribology Transactions*, 4: 470–480. DOI: 10.1080/10402000802687940.

Maskaev A., Mankovskaya N., Lendel I., Fedorovskii T., Simurova E., Terenteva V., 1971. Preparation of 12-hydroxystearic acid, the raw material for plastic greases. *Chemistry and Technology of Fuels and Oils*, *Springer, New York*.

Mazurkiewicz A. (przewodniczący zesp.) i zespół, 2006. Nanonauka i nanotechnologia. Narodowa strategia dla Polski. *Raport Ministerstwa Nauki i Szkolnictwa Wyższego, Warszawa.*

Mencel K., Kelar K., Jurkowski B., 2009. Technologia otrzymywania nanokopozytów poliamidowo-montmorilonitowych. *Czasopismo Techniczne*, 3: 229–235.

Molenda J., Grądkowski M., Urbański A., 2001. Urządzenie do oceny konsystencji plastycznych środków smarowych. *Problemy Eksploatacji*, 2: 155–165.

Molenda J., Samborski T., Wojutyński J., 2003. Penetrometry do badania właściwości reologicznych smarów plastycznych. *Problemy Eksploatacji*, 3: 111–125.

Molenda J., Świgoń K., Urzędowska W., Sacha D., 2010. Korelacja wyników badań stabilności oksydacyjnej biopaliw silnikowych uzyskanych za pomocą testu Rancimat oraz Petrooxy. *Nafta-Gaz,* 10: 922–926.

Mortier R.M., Fox M.F., Orszulik S.T., 2010. Chemistry and Technology of Lubricants. *Springer, Berlin.*

Nora A., Szczepanek A., Koenen G., 2005. Metallic Soaps. *Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim.*

Pagacz J., Pielichowski K., 2007. Modyfikacja krzemianów warstwowych do zastosowań w nanotechnologii. *Czasopismo Techniczne*, 1: 133–147.

Piecyk L., 2006. Nanokompozyty termoplastyczne. *Tworzywa sztuczne*, 2: 20–25.

Pogosyan A.K., Martirosyan T.R., 2008. Tribological properties of bentonite thickener-containing greases. *Journal of Friction and Wear,* 29(3): 205–209.

Razak I.H.A., Ahmad M.A., Puasa S.W., 2019. Tribological and Physiochemical Properties of Greases for Rail Lubrication. *Tribology Online*, 14(5): 293–300. DOI: 10.2474/trol.14.293.

Rizvi S.Q.A., 2009. A Comprehensive Review of Lubricant Chemistry, Technology, Selection, and Design. *ASTM International, Baltimore.*

Rudnick L.R., 2009. Lubricant Additives: Chemistry and Applications. *CRC Press, London.*

Sinha Ray S., Okamoto M., 2003. Polymer layered silicaten a nocomposites are view from preparation to processing. *Progress Polymer Science,* 28: 1539–1549. DOI: 10.1016/j.progpolymsci.2003.08.002.

Szmatoła M., Chrobak J., Grabowski R., Iłowska J., Woch J., Szwach I., Drabik J., Wrona M., Kozdrach R., Orlińska B., Grymel M., 2018. Spectroscopic methods in evaluation of modified vegatable base oils from Crambe abyssinica. *Molecules,* 23: 3243–3250. DOI: 10.3390/molecules23123243.

Wietelmann U., Bauer R.J., 2000. Lithium and Lithium Compounds. *Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH.*

Rafał KOZDRACH MSc.
Research Network Łukasiewicz – Institute for Sustainable Technologies
K. Pulaski Street 6/10
26-600 Radom
E-mail: *rafal.kozdrach@itee.radom.pl*