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APPLICATION OF VEGETABLE OILS FOR THE FRICTION PAIR MODIFICATED WITH A BORON

ZASTOSOWANIE OLEJÓW ROŚLINNYCH W MODYFIKOWANYCH BOREM WĘZŁACH ŚLIZGOWYCH

Key words: vegetable oils, friction, boron surface layer.

Abstract In the article, the results of the conducted research were discussed, and the aim was the evaluation of the characteristics of the operation of sliding pairs when vegetable oils are used for lubrication. Particularly, friction pairs with hard layers containing boron were taken into account. For comparison, two of the most common vegetable oils were used during the tests. Rapeseed oil was chosen, since it is most frequently applied in Europe, soybean oil was chosen due to its occurrence in North American areas. The oils are also applied in industry for commercial aims as oil bases for lubricants. The products based on vegetable oils can constitute an alternative for those of mineral origin. However, vegetable oils are characterized by different properties than mineral oils. The most essential issue is the fact that biolubricants are free of sulphur-containing compounds that can have an unfavourable influence on the health of human beings. The wear measurements were conducted on a block-on-ring test stand T-05. In the sliding pair lubricated with vegetable oils, steel specimen interacted with a counterpart made of bearing alloy. In the second variant of a friction pair, a steel ring specimen with a boronized surface layer was used. The changes of the surface roughness of the specimen and counterpart during operation were evaluated. In the comparative evaluation, the best results were obtained choosing the sample with the hard layer lubricated with soybean oil. In this case, the observed wear of the surface of sliding pairs was the lowest. The lowest friction force and the lowest temperature of the elements of the friction pair also corresponded to this. The application of the TiB_2 layer allows reducing the wear of both the sample with the layer and the counterpart with the bearing alloy layer.

Słowa kluczowe: oleje roślinne, tarcie, modyfikacja borem.

Streszczenie W artykule omówiono wyniki przeprowadzonych badań, których celem była ocena charakterystyki pracy węzłów ślizgowych, do których smarowania zastosowano oleje roślinne. Podczas testów w celu porównania wykorzystano dwa najbardziej rozpowszechnione oleje roślinne. Wybrano jako najczęściej znajdujący zastosowanie na terenach europejskich olej rzepakowy oraz wykorzystywany w warunkach amerykańskich olej sojowy. Oleje te znajdują zastosowanie również w przemyśle do celów komercyjnych jako bazy olejów smarowych. Produkty oparte na olejach roślinnych stanowić mogą alternatywę dla tych pochodzenia mineralnego. Oleje roślinne charakteryzują się jednak odmiennymi właściwościami niż oleje mineralne. Najbardziej istotną kwestią jest to, iż nie zawierają one składników mogących niekorzystnie oddziaływać na zdrowie istot żywych. Pomiary sił tarcia i zużycia węzła smarowanego tymi olejami wykonano na testerze typu klocek-rolka T-05. W smarowanym olejami roślinnymi węźle współpracowała pierścieniowa próbka stalowa z przeciwpróbką pokrytą stopem łożyskowym. W drugim wariancie pary ciernej zastosowano pierścieniową próbkę stalową, na której zastosowano borowanie w postaci warstwy TiB_2. Ocenie poddano zużycie współpracujących elementów oraz zmiany chropowatości ich powierzchni w trakcie pracy. W badaniach porównawczych najlepsze rezultaty uzyskano dla próbek z naniesioną powłoką TiB_2 smarowanych olejem sojowym. W tym przypadku zużycie elementów pary ciernej było najmniejsze. Odpowiadały temu również najmniejsze wartości siły tarcia i temperatury podczas pracy.

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INTRODUCTION

Lubrication is an excellent way to reduce friction, which is suitable for engines and machinery. The presence of lubricants in machines and engines can overcome the economic implications of wear for the manufacturing industry. A traditional lubricant, petroleum, has been commonly used as the lubricant for most industrial mechanics and engines. However, the use of mineral oil poses a risk to the environment and safety due to its degree of toxicity and high flammability. Therefore, scientists are searching for optional lubricants in order to replace the use of conventional oil lubricants. Technical oils in common use, generated from petroleum, constitute a serious ecological problem due to their toxic properties. The risks associated with their application appear both during production and application. In both cases, some leaks out-of-control can occur. Further utilization of used oils also constitutes a large problem. It is estimated that 10 million tons of petroleum products penetrate into the natural environment every year **[L. 1–4]**. The detrimental effect on the environment can result from both the oil base and the packs of additives used to modify the properties of final products. In the compositions of lubricants, organic sulphur compounds are used because of their anti-friction and anti-wear properties. However, environmentally friendly lubricants should not contain mutagenic or carcinogenic substances, nor chlorine or heavy metal nitrates **[L. 5, 6]**.

For ecological reasons, attempts are undertaken to use more environmentally friendly liquids. Products based on vegetable oils can be an alternative to fossil oils. There is a clear tendency for the practical application of the environmentally friendly products from plant oils that biodegrade in a short time. Besides their traditional use, the oil plants constitute a significant supplement of the base of industrial products in technological applications **[L. 7–10]**. It is also very important that oil plants can be cultivated on the grounds of limited agriculture usability for technological purposes, for example, on industrial or contaminated land. Widening a range of the use of vegetable oils makes their tribological properties become essential in many cases, because they may determine the work of friction nodes lubricated with them **[L. 11–15]**.

Vegetable oils had been used as lubricants for machinery and transportation vehicles for a prolonged period of time before petroleum resources were discovered. Petroleum, primarily cheaper and of improved performance, quickly replaced vegetable oils as the lubricant. Now, owing to major factors such as environmental concerns, increased petroleum costs, and decreased petroleum reserves, vegetable oils are gaining popularity as lubricating agents. The products based on vegetable oils can be an alternative to petroleum-based products. However, vegetable oils are characterized by other qualities than mineral oils. The physical and chemical properties of vegetable oils depend on the composition of the fatty acid mixture. Adsorption on the lubricated surface and chemical reactions are two main factors that influence the boundary lubrication properties of oils. The first one describes the ability of the oil to be adsorbed onto friction surfaces during a tribological process. Adsorption occurs as a consequence of the interaction of the functional groups of the vegetable oils and the friction surfaces. The second factor deals with the tendency of the vegetable oils to undergo a chemical reaction. The structure with long fatty acid chains and the presence of polar groups in the vegetable oils determine lubricating properties. The triacylglycerol molecules in vegetable oils orient themselves with the polar end at the solid surface. Thanks to this, monomolecular or multimolecular layer is created on lubricated surfaces. The aim of the paper was to evaluate the operation characteristics of the sliding pairs with boronized hard surface layers lubricated by chosen vegetable oils.

VEGETABLE OILS

Vegetable oils are known as eco-friendly lubricants due to their many advantages, involving non-toxicity, high biodegradability, good low temperature properties, renewable resources, and low costs. A significant amount of research and improvement has been carried out on vegetable oils used in industry. Out of vegetable oils, soy bean oil is the one produced most in the world. The vegetable oils have found wide applications as hydraulic fluid and lubricants, while reducing the amount of carbon dioxide in the atmosphere that contributes to the greenhouse effect. The environmental relevance of oleochemicals in comparison to petrochemicals was discussed in the beginning of the 21st century by A. Willing **[L. 16]**. The ecotoxicological properties and the biodegradability of oleochemical esters were presented, as well. Moreover, the ecological properties of the oleochemical esters were discussed with regard to existing environmental classification and labelling systems. Willing also described the principles of their ecological assessment. Biodegradability values were compared to the overall chemical composition and the main physical properties of base oils by F. Hausa **[L. 17]**. He noticed that biodegradability decreased with increasing levels of aromatic and polar compounds in the oils. For most oils, the biodegradation percentage increased with the viscosity index, but it decreased with the kinematic viscosity. There are a number of methods that can be used to increase the stability of vegetable oils. In order to enlarge the stability of vegetable oils at high temperatures and the presence of an oxidizing agent, the oils can undergo the processes of epoxidation and hydroxylation. These reactions resulted in obtaining a biopolyol substituted by isopropyl alcohol **[L. 18–20]**. A lot of development and research is conducted to improve the physicochemical properties of vegetable oils so that they can compete with petroleum-based lubricants. The number of plant-based lubricants have been estimated for various sectors of industry.

SURFACE LAYER WITH BORON

The demand for the increased performance of machine components has forced the use of various substitute materials for sliding pairs, which is especially significant in the case of mixed friction conditions.

The modification with boron can be carried out in various ways using different technologies, e.g., the creation of coatings containing boron, diffusion of boron into the surface layer, and an alloy addition in metallurgical processes **[L. 21]**.

Boronizing as a thermochemical process is broadly used for boride-type coatings. Borides formed on the steels surfaces have an influence on material corrosion resistance, wear resistance, and surface hardness **L. 22, 23]**. The tribological properties of these layers depend on a physical state of boride source applied in the process, its temperature, treatment time, and the properties of the boronized material **[L. 24]**. This is the reason that boronizing processes are used on surface layers characterized by high hardness, improved wear resistance, a low friction coefficient, and no tendencies towards cracking **[L. 25, 26]**. Properties of metal borides coatings can be very useful. They may be used under severe operating conditions; whereas, conventional solutions exhibit performance difficulties at larger loads, higher speeds, and higher temperatures on low cost engineering materials.

Titanium diboride (TiB_2) is a transition metal based on refractory ceramic with a hexagonal structure and a metallic chemical bonding character. TiB_2 has obtained a growing interest from industry and researchers due to its unique functional properties, e.g., high hardness, high wear and corrosion resistance, and a high melting point **[L. 27, 28]**. Titanium diboride is a material which has a great potential for tribological applications. The modification of the material with boron should be selected upon the required operating conditions and characteristics of the kinematic sliding pairs **[L. 23, 29]**. Thus, it is crucial to determine the influence of the elements of sliding pairs modified with boron on the operating conditions and wear of the pairs during lubricated friction.

EXPERIMENTAL DETAILS

The main goal of the present work was to study the application of vegetable oils for the lubrication of sliding pairs with a hard surface layers containing boron. Within the experiment, the tribological behaviour of a TiB_2 coating in sliding applications with a bearing alloy was evaluated. Thus, it was essential to determine the influence of the TiB_2 coating modification of the sliding pair elements on the operating characteristics and wear under lubrication conditions. The tests were carried out under limited lubrication with the use of two chosen vegetable oils in order to determine the impact of the lubricant on the processes of friction and wear. The tribological tests were conducted on a T-05 block-on-ring tester (**Fig. 1**). Tested sliding pairs were lubricated with vegetable oil.

The ring of a 35 mm diameter interacted with a block of 6.35 mm in width during the tests. In the tests, the intensity of the wear of the specimen and counter specimen was assessed, as well as the changes of roughness parameters on their surfaces. The tests were carried out with two vegetable oils mostly used in industry: rape oil and soybean oil. These oils can be used, among others, as base oil for lubricant formulation. A glass capillary viscometer was applied for measuring kinematic viscosity. However, the pycnometer method was used for measuring the density of lubricating oils. The characteristics of these vegetable oils are presented in **Table 1**.

In the experiments, ring specimens from 46Cr2 steel with a borided surface layer were used. The ring specimens were covered with the TiB_2 coating using PVD method. The conditions of the process were as follows: process time – 40 min at a temperature of 400°C, and pressure in the ionization chamber – 2.5 x 10–3 MPa. The layer obtained on the ring had the thickness of 3 µm and a hardness of 3000 HV.

During the tests, heat treated ring specimens from 46Cr2 steel were also used. The ring hardness amounted to 38 HRC. The obtained layers were then matched under test conditions with counterparts made from AlSn20 bearing alloy. The counterparts' hardness amounted to 35 HB.

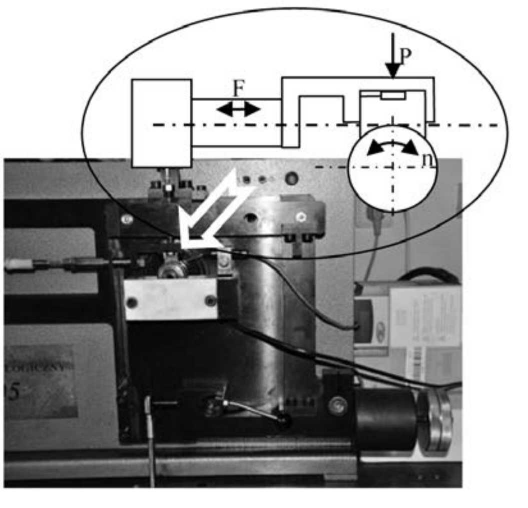

Fig. 1. T-05 test stand, which was used for friction measurements and schematic representation of measurement way

Rys. 1. Tester T-05 wykorzystany do pomiarów oraz schemat sposobu pomiaru

Table 1. Characteristics of the composition of examined vegetable oils
Tabela 1. Charakterystyka zastosowanych olejów roślinnych

Oil	Rapeseed oil	Soybean oil
fatty acid	percentage of fatty acid %	percentage of fatty acid
C12:0	-	0,1
C14:0	0.2	0.2
C16:0	2.5–7.0	8–13
C16:1	0.6	0.2
C17:0	0.3	0.1
C17:1	0.3	0.1
C18:0	0.8–3.0	2–5
C18:1	51–70	17–28
C18:2	15–30	49–59
C18:3	5–14	5–11
C20:0	0.2–1.2	0.6
C20:1	0.1–4.3	0.5
C20:2	0.1	0.1
C22:0	0.6	0.7
C22:1	2.0	0.3
C22:2	0.1	-
C24:0	0.3	0.5
C24:1	0.4	-
density [kg/m^3]	918	921
kinematic viscosity [mm^2/s]	67	79

RESULTS AND DISCUSSION

The influence of the vegetable oil used for the lubrication of sliding pairs on friction force and its temperature was evaluated. Both chosen oils (rapeseed and soy bean oil) were applied for the lubrication of the ring with a TiB_2 surface layer and a ring without it. In both cases, the block surface contacting with ring in the tester was covered with bearing alloy. The obtained results were juxtaposed in **Figure 2**. The measurements made on block-on-ring tester indicate that the soy bean oil allowed obtaining friction force about 15% lower. Lower values of the friction force could be observed both in the case of lubricating the ring with a TiB_2 layer and without it. However, for the TiB_2 layer and applied soy bean oil, friction forces were the lowest out of all conducted measurements. In this case, the lowest temperatures during operation were also recorded. The measured temperature was almost 10% lower compared to the highest one observed during lubrication of the ring without a layer and with rapeseed oil.

In **Figure 3**, the wear of ring samples are shown. Both for the block and for the ring, the mass decrement of the tested elements was the smallest for the TiB_2 layer, as can be seen in the figure. Both for the rapeseed and soybean oil, the wear was four times higher in the case of the operation of the ring without surface layer than the one with the layer of TiB_2. In the case of the ring with the TiB_2 layer, the noticeable wear could be observed during the first two hours of the test. The largest wear was recorded in the case of the application of rapeseed oil for

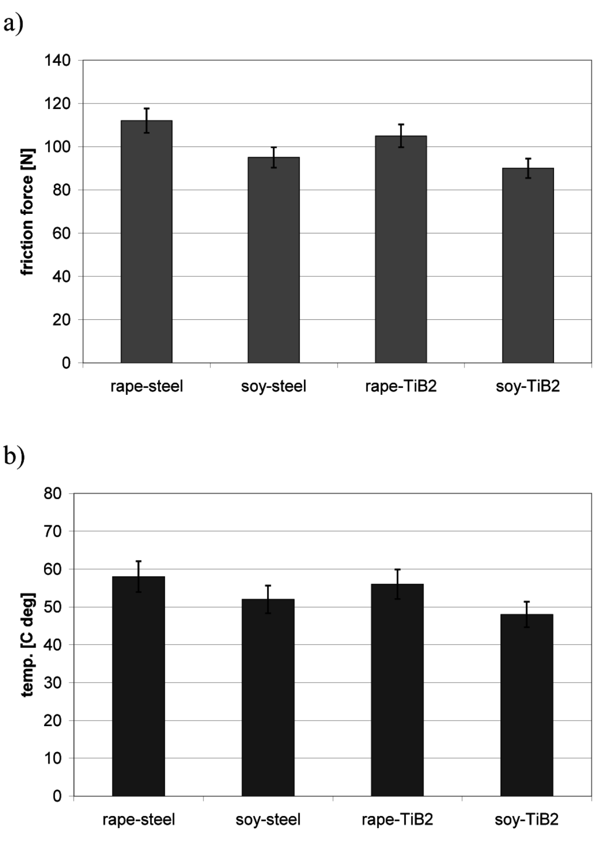

Fig. 2. The influence of oil type (rapeseed and soybean oil) on friction forces and temperature of the elements of sliding pairs: steel-AlSn20, TiB_2 layer – AlSn20
Rys. 2. Wpływ rodzaju oleju (olej rzepakowy i olej sojowy) na siłę tarcia i temperaturę pracy par ślizgowych: stal–AlSn20; warstwa TiB_2–AlSn20

lubricating the steel ring without the layer. In the case of the ring with the TiB_2 layer, the wear is the slightest, irrespective of the used oil. The most even wear during the course of the test could be observed when the steel ring without the layer was used and rapeseed oil was used for lubricating. However, the differences in wear when the same elements were lubricated with soybean oil are not significant and reach up to 5%.

The changes of the roughness on the block and ring surfaces during the test described with the Ra and Rz parameters are shown in **Figs. 4** and **5**. During the test, no significant changes of Ra and Rz values were observed. Only in the first hour of the test, the changes appeared due to the wear of the elements. In order to measure the roughness of the surface of tested elements, the test process was stopped. In **Fig. 5**, in the case of rape oil, we can see a temporary change in the value of the Rz specimen. However, it can be explained by a necessity of a renewed assembly of the tested elements.

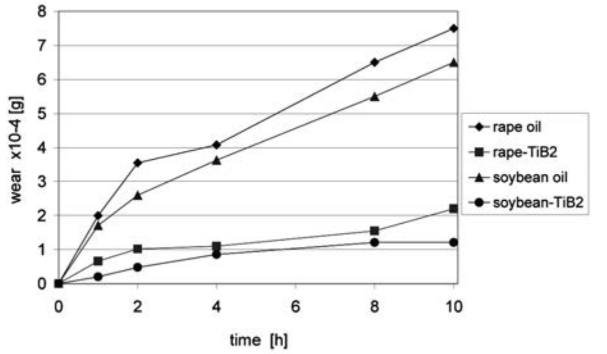

Fig. 3. Specimen wear during tests, elements of sliding pairs: steel-AlSn20, TiB_2 layer – AlSn20

Rys. 3. Zużycie próbki podczas testu par ślizgowych: stal––AlSn20; warstwa TiB_2–AlSn20

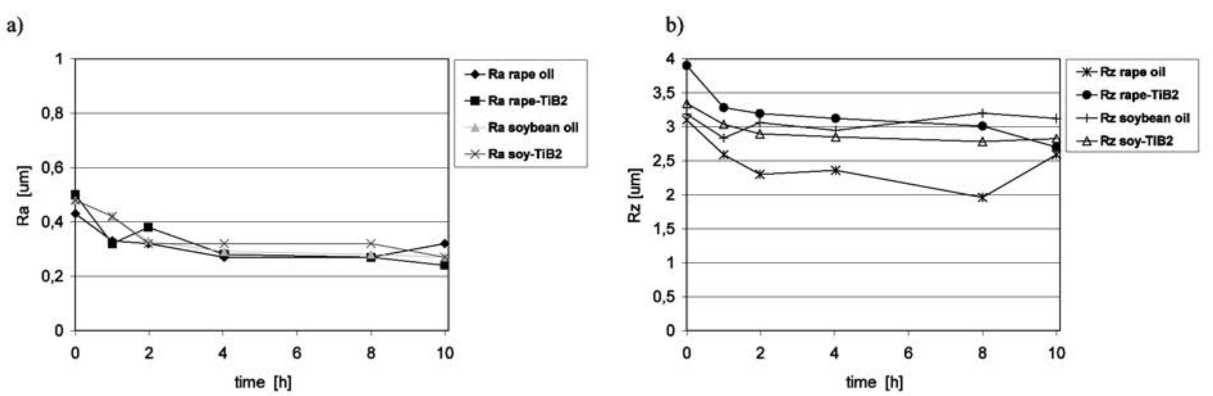

Fig. 4. Changes of specimen surface roughness during tests, elements of sliding pairs: steel-AlSn20, TiB_2 layer – AlSn20

Rys. 4. Zmiany chropowatości powierzchni próbki podczas testu par ślizgowych: stal–AlSn20; warstwa TiB_2–AlSn20

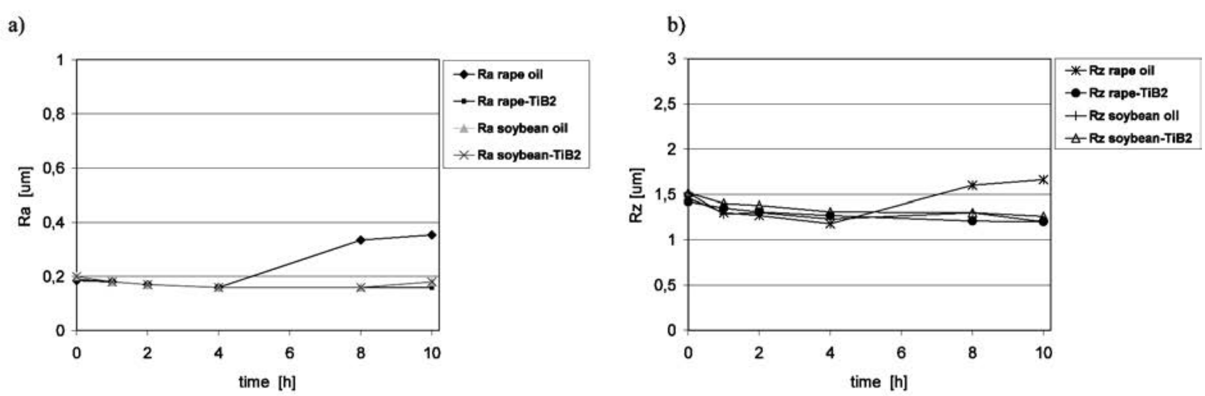

Fig. 5. Changes of counter specimen surface roughness during tests, elements of sliding pairs: steel-AlSn20, TiB_2 layer – AlSn20

Rys. 5. Zmiany chropowatości powierzchni przeciwpróbki podczas testu par ślizgowych: stal–AlSn20; warstwa TiB_2–AlSn20

The measured parameters of surface roughness indicate the intensity of friction and its influence on shaping the geometric structure of sliding pairs. As a result of the processes occurring within the friction area, changes of the geometric structures of both interacting elements occur. The created-geometric structure of the surface has to be the most suitable for friction conditions. As a result of the changes of the surface roughness, optimal operating conditions may be obtained. Such an optimal surface structure allows for the diminishing of wear intensity. In pairs where this kind of relationship does not exist and the load on the contact surface is large, it is not possible to create a state of equilibrium. In such cases, the destruction of the surface of sliding pair occurs **[L. 31, 32]**. Sliding pairs that exhibited the tribochemical equilibrium generate optimal conditions for their further operation. The observed changes are the result of physiochemical processes and the changes in the micro-geometry of the friction surface due to the adaptation of the system to the conditions of external load. In the sliding pairs, which exhibit a significant decrease in the friction coefficient, the improvement of the friction conditions depends on the increase of the effectiveness of the lubrication by the oil, due to the existing tribochemical changes. These phenomena result from the elementary wear processes occurring within the contact area of the sliding pair on the elementary surface of the interacting layers. The lubrication factor is crucial for these processes, since it can create favourable friction conditions, depending on its transformation. These changes contribute to generating boundary layers on the surface, which are either highly resistant to ruptures or quickly destroyed under variable operating conditions. Among these are the effects of wear products on frictional surface layers, and material transfer **[L. 32]**. The stabilization of the temperature indicates the adaptation of the pair to the existing load and the generation of stable anti-wear and anti-seizure layers **[L. 33]**. In boundary lubrication conditions, the destruction of a solid-like film adsorbed on the contact surfaces is the result of intense suppression of the liquids under higher load. The same effect can occur when the oil viscosity and sliding speed are very low **[L. 34, 35]**. The double bonds existing in the unsaturated fatty acids of vegetable oils are prone to bond breaking at high temperatures. Although the long covalently bonded hydrocarbon chain is capable of reducing the friction coefficient, the increase of wear can occur.

In general, lubricants based on pure or chemically modified vegetable oils are found to have superior lubricity than mineral-based oil, especially on boundary lubrication regimes as reported in several studies **[L. 36]**. The main reason for this is the fact that fatty acid molecules within the vegetable oils can react with metal surfaces to form a low shear strength metallic soap layer. The formation of iron stearate layer from the reaction of iron from metal surface with free fatty acids like stearic acid can be an example of this simple reaction. The metallic soap layer can effectively reduce the friction coefficient between surfaces **[L. 37]**. Oil containing fatty acids with long chains (C18 and above) showed better anti-wear and lubricity properties compared to oils containing shorter fatty acids chain lengths. This is due to vegetable oils containing a high percentage of oleic acid (C18:1), which are capable of maintaining low friction coefficient values and low wear. This oleic acid can form a monolayer that can minimize the asperity contact and protects the metallic surfaces during an operation **[L. 38]**. In some cases, an increase in the amount of wear on sliding interfaces was reported when bio-based lubricants were tested. In operating conditions, continuous sliding motion will result in continuous removal of the protecting metallic soap film. This film transformation is then repeated again and again by the same chemical reaction, resulting in increased wear. The increased wear is also caused by the corrosive effect of peroxides and free fatty acids as products of oxidation **[L. 39]**. The increase of the wear on steel surfaces in conditions of boundary lubrication is explained by the fact that, at higher temperatures, the bio-based lubricant can easily oxidize, leaving a layer of corrosive products on contact surfaces. However, this layer of corrosive products can also bring benefits, because, during sliding interaction, this layer is removed instead of the surface materials **[L. 40]**. The presence of a polar group with a long hydrocarbon chain makes vegetable oil amphiphilic surfactant by nature; therefore, it can be used as a lubricant in boundary conditions. The molecules have strong affinity for metal surfaces and interact easily with them. On metal surfaces, the long hydrocarbon chain is oriented away from the surface and can form a monomolecular layer with excellent boundary lubrication properties. Analysing the composition of the tested oils, we can notice that both rape and soybean oil contain very small quantities of fatty acids with a large number of carbon atoms, from C20 and more, and with multiple carbon bonds, like Arachidic acid (C20:0), Eicosanic acid (C20:1), Behenic acid (C22:0), and Erucic acid (C22:1). However, the differences in the percentage share of the mentioned fatty acids in studied oils reach 100%. Fatty acids with multiple carbon bonds, such as C18:1 and C18:2, have the highest percentage.

SUMMARY AND CONCLUSIONS

The products based on vegetable oils can constitute an alternative for those of mineral origin. For comparison, two most common vegetable oils were used during the tests. Rapeseed oil was chosen since it is most frequently applied in Europe, and soybean oil was used due to its occurrence in North American areas. On the grounds of test results, it can be stated that, regarding tribological properties, vegetable oils would be a good alternative to the mineral oil bases.

On the basis of these measurements, the results of this study can be summarized as follows:

In the comparative evaluation, the best results were obtained choosing the sample with the hard layer lubricated with soybean oil. In this case, the observed wear of the surface of sliding pairs was the lowest. The lowest friction force and the lowest temperature of the elements of friction force also corresponded to this. The application of a TiB_2 layer reduced the wear of both the sample with the layer and the counterpart with the bearing alloy layer. In the case of the TiB_2 layer, the change of the vegetable oil used for lubricating caused the change of wear solely by 5%.

The surface roughness shaped in the friction pair depends on the initial roughness, friction conditions, and the applied surface treatment. The registered trends do not lead to the decrease of surface roughness, but they rather help to create an optimal geometrical structure and friction conditions for a given pair.

During the conducted research, two vegetable oils were used. They were rape oil and soybean oil. The oils were characterized by different chemical composition. The physical and chemical properties of vegetable oils depend on the composition of the fatty acid mixture. Analysing the composition of the tested oils, we can notice that both rape and soybean oil contain very small quantities of fatty acids with a large number of carbon atoms, from C20 and more, and with multiple carbon bonds, like Arachidic acid (C20:0), Eicosanic acid (C20:1), Behenic acid (C22:0), and Erucic acid (C22:1). However, the differences in the percentage share of the mentioned fatty acids in studied oils reach 100%. Fatty acids with multiple carbon bonds, such as C18:1 and C18:2, have the highest percentage.

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