ISSN 0208-7774 TRIBOLOGIA 2/2021 p. 7–20
DOI: 10.5604/01.3001.0015.5859

Marcin FRYCZ[*], **Mateusz LABUDA**[**]

AN ANALYSIS OF THE INFLUENCE OF CARBON NANOPARTICLES ADDITIVE ON SELECTED PROPERTIES OF LUBRICATING OILS

ANALIZA WPŁYWU DODATKU NANOCZĄSTEK WĘGLA NA WYBRANE WŁAŚCIWOŚCI OLEJÓW SMAROWYCH

Key words: properties of the lubricating oils, carbon nanoparticles, friction coefficient.

Abstract: This paper presents the results of an analysis of the influence of the addition of various types of carbon nanoparticles on selected essential physical and operational properties of lubricating oils. Two selected oils, i.e. the mineral base oil without additives and the typical marine lubricating circulating oil Marinol RG 1240, were modified with the addition of shungite nanoparticles, graphite nanotubes, and C_{60} fullerenes. The mass fraction of modifiers was 0.2% wt for each of the additives. As part of the experimental tests, measurements were made of the impact of the above-mentioned modifiers on the change in the value of the ignition temperature of oils, the effect on the changes in the value of the dynamic viscosity coefficient in the aspect of changes of temperature and shear rate, as well as the impact on the changes in the friction coefficient and the size of the wear size scar. These tests were carried out on an EraFlash automatic apparatus for determining ignition temperature using the closed cup method, with a Haake Mars III research rheometer, and a T-02U tribometer with a four-ball head.

Słowa kluczowe: właściwości olejów smarowych, nanocząstki węgla, współczynnik tarcia.

Streszczenie: W niniejszej pracy zaprezentowane zostały wyniki analizy wpływu dodatku różnego rodzaju nanocząstek węgla na wybrane istotne właściwości fizyczne i eksploatacyjne olejów smarowych. Dwa wybrane oleje, tj. mineralny olej bazowy nie zawierający dodatków uszlachetniających oraz typowy morski smarowy olej obiegowy Marinol RG 1240, zostały zmodyfikowane dodatkiem nanocząsteczek szungitu, nanorurek grafitu oraz fullerenów C_{60}. Udział masowy modyfikatorów wynosił 0,2% wt w przypadku każdego z dodatków. W ramach badań eksperymentalnych dokonano pomiarów wpływu wymienionych modyfikatorów na zmianę wartości temperatury zapłonu olejów, wpływu na zmiany wartości dynamicznego współczynnika lepkości w aspekcie zmian temperaturowych, jak również szybkości ścinania, a także wpływu na zmiany współczynnika tarcia i wielkości śladu zużycia. Badania te zostały przeprowadzone odpowiednio na automatycznym aparacie do wyznaczania temperatury zapłonu EraFlash metodą tygla zamkniętego, reometrze badawczym Haake Mars III oraz tribometrze z głowicą czterokulową T-02U. Uzyskane w badaniach eksperymentalnych wyniki zostały poddane analizie, zostały również poczynione obserwacje oraz wyciągnięte wnioski dotyczące wpływu nanomodyfikatorów węgla na wybrane właściwości olejów w szczególności w kontekście ich potencjalnego zastosowania w olejach smarujących.

INTRODUCTION

The aim of this paper was to determine the effect of the addition of carbon nanoparticles that have various morphological forms on selected properties of lubricating oils used in marine technologies. The examined supplements were fullerenes C_{60} nanoparticles, single-layer carbon nanotubes, and amorphous natural carbon variant – type 1 shungite.

---

[*] ORCID: 0000-0001-8603-0523. Gdynia Maritime University, Faculty of Management and Quality Science, 81-87 Morska Street, 81-225 Gdynia, Poland, e-mail: m.frycz@wm.umg.edu.pl.

[**] Gdynia Maritime University, Faculty of Management and Quality Science, 81-87 Morska Street, 81-225 Gdynia, Poland.

Within the tribomechanical systems of the engines and other ships' devices, friction processes take place, which result in current energy loses and long-term losses caused by wear. Both have a negative impact on the economic balance of operation processes as well as on the reliability and durability of elements, assemblies, and entire machines. The most common solution to the problem of anti-wear is to improve the working surfaces of components operating in conditions of intense frictional impact. That usually means using materials and surface layers that have increased wear resistance. A different strategy is to create such friction conditions within tribomechanical nodes that produce lower friction forces, which can lead to lower wearing intensity. This can mean using lubricants that have increased anti-friction and anti-wearing properties.

Selecting and using specific lubricant oils in marine technologies is, in practice, under the general economical balance of operation process' pressure, that is why the most commonly chosen and used are relatively cheap mineral oils in this particular transport branch. On the other hand, the useful life of circulating oils is currently estimated up to 25,000 hours for newer two-stroke engines **[L. 1]**, which makes the use of modern modifiers of these oils in the field of anti-friction and anti-wear properties worth considering. According to the analysis of research conducted so far **[L. 2–11]**, additives with such potential may be carbon nanoparticles. The intention of this study is to give hints as to which of these modifiers have a chance to effectively arouse the interest of the owners of the world's maritime transport fleet.

CARBON NANOPARTICLES CHARACTERISTICS

Carbon atoms tend to form differently in terms of the number of atoms in the molecule, but also the structures that bind these atoms in allotropic forms. Two of them were known to mankind from time immemorial, and their physical and chemical properties can be successfully considered as thoroughly known also in the context of tribological properties. These are, of course, diamond, and graphite. However, relatively recently, since 1985, the arsenal of allotropic forms of carbon was enriched with newly discovered structures. The enormous utilitarian potential of these new forms of carbon was immediately noticed, and intensive research is underway all over the world into the unique properties of these carbon structures. Previous positive experiences with the use of graphite also prompted the undertaking of tribological studies with the use of new allotropic forms of carbon in this context.

The fullerene C_{60} – used in the present study as nanomodifiers, belonging to the regular fullerenes, is the most classic form of such carbon molecules. It is composed of 60 carbon atoms in the shape of a truncated icosahedron formed with conjugated 6-atom rings. Both their physical properties, in particular their regular, almost spherical shape, but also excellent thermal conductivity and chemical properties similar to those of aromatic hydrocarbons, make fullerenes of this type an addition of lubricants that determine anti-friction and anti-wear properties.

Carbon nanotubes, the second of the tested nanomodifiers, are usually graphite cylinder-shaped structures with a diameter from a few to a dozen nanometres and many times greater length, although their structure may differ significantly depending on the method of folding a monatomic graphite plane (single and multilayer nanotubes, nano-coils, nanotorus or fullerites). The carbon tubes used in this study are single-layer open top and hollow structures with a diameter of 5nm to 10 nm with a purity of 99.8% produced by the Belarusian Institute of the Heat and Mass Transfer of V. Laikov in Minsk. These nanotubes are characterized by very good mechanical properties, especially tensile strength, but also high flexibility and elasticity, which translate into good bending and torsion strength. They also exhibit, as in the case of fullerenes, great thermal, and heat properties. These features make carbon nanotubes a promising modifier for lubricating oils operating under high mechanical and thermo-chemical loads.

The last of the tested nanomodifiers is a natural amorphous form of carbon – shungite. The term nano- in this case refers not so much to carbon as such, but to the naturally occurring fullerenes and fullerenomorphic structures of various kinds. The molecular structure of shungite is mainly solid non-crystallized carbon, and it can be compared with that of graphite or soot. A characteristic feature is the layers of hollow spheres resembling fullerenes. Their size is from 10 nm to 30 nm. The spheres form clusters of several dozen to several hundred carbon atoms. The shungite used in the research was its I-type, which means that the carbon content in the sample exceeded 98% (the product was modified for research purposes by the above-mentioned Institute in Minsk). The content of fullerenes in the sample is unknown due to the natural origin of the product. Previous studies with the use of shungite confirm its adsorption, catalytic, and oxidation properties **[L. 12, 13]**. Considering shungite as a potential enriching additive to lubricating oils, one should pay attention to its anti-corrosion properties, high mechanical and abrasion resistance, and the aforementioned adsorption properties.

LITERATURE ANALYSIS

Literature studies based on the research conducted so far clearly indicate a significant and beneficial effect of the addition of carbon nanomodifiers on the properties of lubricating oils. In simple terms, the lubrication mechanism is essentially based on two basic properties of lubricants, i.e. their viscosity and lubricity. The former plays a decisive role in the conditions of fluid friction, when the friction surfaces are separated from each other by a layer of lubricant under pressure. This pressure balances the external loads and the lubricant layer forms the load-bearing carrier layer. With such lubrication, the fluid resistance to movement is determined by the internal friction of the liquid, i.e. its viscosity, and is a combination of the resistance to mutual sliding of the layers of lubricant along the thickness of the lubricating layer. The rheological properties of the lubricant determine its ability to create a carrying layer of the required minimum thickness, ensuring conditions for a smooth lubrication characterized by low coefficients of friction, which, for the friction nod elements, means low energy losses, resistance to wear, producing high durability.

The significance of the second important property, i.e. lubricity, increases when the friction conditions change and we deal with mixed friction – a combination of fluid and boundary friction. The significance of the second important property, i.e. lubricity, increases when the friction conditions change and we deal with mixed friction – a combination of fluid and boundary friction. It is precisely this ability to maintain this boundary layer under varying frictional conditions that determines the high desired lubricating properties of the agent used. The presence of such a layer is of key importance for reducing the friction force as compared to the dry friction conditions (from 2 to 10 times), which may translate into a reduction in wear up to 100 times **[L. 14]**. The specific strength of the surface layer depends on the presence of active molecules in the lubricant, their number, but mainly their physicochemical properties. The role of these molecules can be played by carbon nanoadditives.

The addition of nanoparticles to the lubricating oil significantly lowers the values of the friction coefficient. It also increases the value of the load carrying capacity in the mechanical system of the friction pair. In the literature on the subject, one can meet with many attempts to explain the essence of the phenomenon of improving lubrication for such modified oils, starting with the postulate of the effect of the impact characteristic for a rolling bearing **[L. 5, 6, 15, 19]**, through the so-called the protective film effect **[L. 2, 16, 17]**, the mechanisms of repairing and filling defects in the surface layer **[L. 18]** and polishing it **[L. 19]**.

The first of them are based on the direct enhancement of the lubricating effect of the lubricant. Nano-particles with a spherical structure, as in the case of fullerenes or shungite, contained in the lubricating oil suspension can play the role of ball bearings between the friction surfaces. This effect is well approximated by the boundary layer model proposed by A.W. Bloom, where the spherical structures of the lubricant's microcells separate the friction surfaces like bearing balls, rolling like a raceway on the surface layer of the lubricant bound to the ground. This model particularly accurately describes the behaviour of hydrocarbons with ring structures, and fullerenes exhibit physicochemical properties similar to them. The addition of fullerenes to the oil, which is a mixture of paraffinic hydrocarbons, could give them the properties characteristic of more expensive synthetic oils consisting of aromatic hydrocarbons in a relatively simple way.

Other additives with planar structures, e.g., nanoflakes, can in turn create a protective film – a quasi-crystalline boundary layer on the friction surfaces. A similar effect may apply to rod structures, such as carbon nanotubes, as long as their chemical properties allow them to form a mono- or polymolecular ordered and oriented perpendicular to the surface of the ciliary layer. Such a mechanism would correspond to the model descriptions initially presented by Karplus or by Hardy and later developed in successive, more and more complex models of creating boundary layers. A necessary condition for the occurrence of such a mechanism would be the tendency of the lubricant composition to create polarized particles that would spontaneously assume the perpendicular orientation to the friction surfaces.

The second of the above mentioned group of phenomena accompanying the presence of nanoadditives in the lubricant and conditioning the improvement of the lubricating effect is of a secondary nature. It is based on the effect of improving the quality of the friction surfaces. Impacts of this kind may be of a dual nature. Or they relate to the deposition of nanoparticles on friction surfaces, which adhere tightly to them and show a repair effect, compensating for the loss of material mass. Or they show the effect of abrasive polishing of the friction surfaces, reducing their roughness and smoothing out unevenness, which significantly facilitates the local conditions of liquid friction.

Regardless of the genesis of the phenomena behind the lubricity improvement effect, literature studies prove the beneficial effect of the addition of fullerenes on anti-wear, tribological, and lubricating properties. This effect applies not only to the fullerenes themselves, but also to chemical compounds similar to them in terms of structure, the so-called IF-, such as tungsten disulphide IF-WS_2, molybdenum disulphide IF-MoS_2 and their derivatives **[L. 8**, **20–21]**. The research on lubricating oils with the addition of fullerenes and graphite **[L. 3]** showed both a significant improvement in friction conditions during the test itself and confirmed the creation of a permanent anti-wear structure on the friction surfaces, which remained after the end of the experiments. Similar results can be found in the work **[L. 22]**, where the influence of nanoadditives with fullerene-like IF-MoS_2 structures on the radical improvement of anti-seize and anti-wear properties was confirmed. The literature analysis shows that the addition of fullerenes does not significantly affect the viscosity of the lubricating oil **[L. 23, 24]**. Regardless of the type of oil and the concentration of additives (the highest tested concentration was 0.2% wt), the change in kinematic viscosity did not exceed 1 mm^2/s. Simultaneously, fullerene C_{60} additive has a favourable effect on the temperature of ignition. SAE 20W50 type oil, having a flash point of 224°C, with the addition of 0.1% wt of C_{60} fullerene, showed 244°C, and with the addition of 0.2% wt, the flash point value increased by another 6 degrees **[L. 23]**.

The effect of shungite as an enriching additive to oils is similar to the addition of fullerenes, but not many studies have been conducted in this area. Among the centres that undertook research on this subject, one can distinguish, among others, research carried out at the Russian Academy of Sciences **[L. 12]**. The study concerned the influence of shungite on the surface condition of balls in the processes of friction and wear in a ball mill. They showed that, although signs of wear normal for the balls used for grinding appeared on the surface of the balls, what is important, a surface layer was formed on the surface of the balls, protecting against further wear. In places where there were scratches on the spheres, the effect of filling them with a mixture was also observed. Even more interesting results were obtained in the studies in which the influence of shungite as one of the components of the mixture enriching the lubricating oil was examined **[L. 13]**. As part of these tests, a significant reduction in the diameter of the wear marks was confirmed as compared to the lubrication with pure oil. The introduction of the shungite additive to the oil also resulted in a slight increase in viscosity (from 11.1 mm^2/s to 11.3 mm^2/s at 100°C) for the oil with the shungite additive content of 1% wt while, the ignition temperature increased by 2 degrees from 213°C to 215°C (measured were performed in an open cup).

Both single-wall and multi-wall carbon nanotubes have become the subject of investigations in terms of their applicability as an additive in lubricating oils, often giving very promising results. The research on the influence of nanoadditives on the properties of oils carried out at the University of Teheran **[L. 23]** showed that the best properties of the oil are obtained with the addition of 0.1% –0.2% wt of multi-wall nanotubes. Viscosity tests at 40°C and 100°C showed no significant changes either for the concentration of 0.1% wt or 0.2% wt. The addition of nanotubes slightly increases the viscosity of the tested oil. At a concentration of 0.2% in wt, it was only 1 mm^2/s. On the other hand, the flash point increased significantly, both for fullerene and polyhedral nanotubes. At a concentration of 0.1% wt, the flash point increased from 225°C to about 237°C for nanotubes and 243°C for the addition of fullerenes.

RESEARCH METHODS

The tests of selected properties of modified lubricating oils were carried out in laboratories of the Faculty of Mechanical Engineering of the Gdynia Maritime University on devices and test stands located there.

In order to determine the ignition temperature, an automatic EraFlash apparatus by Eralytics was used to determine this temperature. This device enables quick and precise determination of the flash point, especially of fuels and oils, in the temperature range -20°C – 420°C with temperature stability of 0.1°C. The tests were carried out in accordance with the ASTM D6450 standard using the closed cup method. A single measurement in this device required only 1 ml of the tested oil.

Rheological tests of changes in the value of the dynamic viscosity coefficient in terms of temperature changes and changes in shear rate were performed on a Haake Mars III rotary rheometer by Thermo Scientific. For the measurement of viscosity changes as a function of temperature, at relatively low shear rate values, a "plate-cone" geometric system was used. In this configuration, thermal stability was ensured by a Peltier system built into the thermostatic jacket, supported externally by a heating and cooling ultra-thermostat. Determination of viscosity changes as a function of shear rate was performed with the use of a "cylinder-cylinder" geometric system thermally stabilized with the use of the already mentioned ultra-thermostat system.

The tribological tests were carried out with the use of the T-02U four-ball head apparatus according to our own research plan.

Additionally, the elemental composition of the tested oils was tested by means of emission spectroscopy on a Spectroil Q100 device according to ASTM D7094 standard, as well as the diameter measurements of the ball wear mark after tribological tests, made with the use of a Zaiss SmartZoom 5 digital measuring microscope.

TESTED OILS AND METHODOLOGY OF SAMPLE PREPARATION

The test samples were prepared with the use of two kinds of oils. The first was the SAE10/95 base oil. It is a mineral, basic oil, obtained from the conservative processing of crude oil, selectively refined, dewaxed, and having no additives. The second oil used as a base for the samples was Marinol RG1240. It is a typical engine oil used to lubricate light fuel marine engines. Unlike the base oil, Marinol oil contains a whole range of additives. These additives have antioxidant, anti-corrosive, anti-wear, and washing-dispersing properties. The purpose of using these oils as a base for samples was to make it possible to compare the effect of the addition of carbon nanoparticles both on the properties of oil, where the only enriching additive are carbon nanoparticles, and on oil, in which carbon nanoparticles constitute an additional modifier of the existing additive composition.

Carbon nanoparticles introduced as oil modifiers, i.e. fullerenes, nanotubes, and shungite, were obtained courtesy of the Institute of Mass and Heat Transfer of V. Luikov in Minsk. Fullerenes C_{60} were certified with a purity level of 99.9%, single-layer carbon nanotubes 99.8%, and Type I shungite was > 98% purified.

For the tests, samples of modified oils with an additive content of 0.2% by weight were prepared. After measuring the appropriate amounts of individual components, they were combined and initially mechanically mixed. The next step was to place the samples in an EMAG Emmi-08ST ultrasonic cleaner. It was aimed at better mixing due to the interaction of frequent and strong ultrasonic waves while heating the samples at 60°C. This process took a dozen minutes, after which the samples were mechanically mixed again. This multi-step mixing process was carried out to obtain the most homogeneous colloidal mixture possible and to avoid aggregation of the additive particles into larger structures. The importance of this process in the context of further research may be proved by the results presented in **[L. 25, 26]** concerning the research on sedimentation and aggregation of particles in such solutions. Additionally, before each single test, the samples were re-mixed both mechanically and with the use of an ultrasonic bath. By the way, observations were made, which showed that the sample modified with carbon nanotubes showed the fastest sedimentation rate and a time interval of several hours was sufficient for noticeable phase separation. Such effects visible to the naked eye did not show for all samples with fullerenes, and samples with shungite only showed to a small extent.

Before starting the proper tests of the properties of the modified lubricating oils, spectrometric tests of the elemental composition of both oils constituting the base of the mixtures were performed. They showed significant differences in the composition of both products, confirmed the basic, raw nature of the base oil and indicated the existence of anti-seize and anti-wear additives already used in sea oil. The obtained results of the elemental composition are presented in **Table 1** below.

Table 1. The content of the elements in the tested oils: base oil SEA 10/95 and Marinol RG 1240
Tabela 1. Zawartość pierwiastków śladowych w badanych olejach: bazowym SAE10/95 i Marinol RG1240

	Trace element content [ppm]					
Type of element	**Ag**	**Al**	**B**	**Ba**	**Ca**	**Cd**
* Base oil	0.31	0.39	0.26	0.09	2.34	0.81
* RG1240	0.34	2.23	2.39	0.22	5220.4	0.78
Type of element	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**
* Base oil	0	0.01	0	0.17	0.29	0.04
* RG1240	0.05	0	0.79	1.12	18.53	3.19
Type of element	**Mo**	**Na**	**Ni**	**P**	**Pb**	**Si**
* Base oil	1.12	1.27	0.54	2.94	0	2.43
* RG1240	9.97	96.62	1.86	1032.06	0.22	10.11
Type of element	**Sn**	**Ti**	**V**	**Zn**	**H**	**C**
* Base oil	0	0.13	0.31	2.33	133200	202600
* RG1240	0	1.98	1.13	756.252	134400	214000

RESULTS AND ANALYSIS

The experimental tests began with the determination of the ignition temperature value of modified oils. The flash point is the lowest temperature at which the vapours of the test substance ignite when an ignition source is applied to them. In the case of the EraFlash device, the source of ignition was a spark, and the point of ignition was characterized by a rapid pressure increase in the closed crucible of the test device. Measurements were carried out on samples of the required standard volume of two millilitres. The temperature increase during the measurement was constant. The device started a spark discharge (ignition source) every 1°C when the temperature was close to the expected value. For each of the oils, three tests were performed and the average results obtained are presented in **Tables 2** and **3** for mixtures with the base oil and Marinol oil, respectively.

Table 2. The values of the ignition temperature of the oils prepared at the base oil
Tabala 2. Wartości temperatury zapłonu dla mieszanin sporządzonych na oleju bazowym

Tested oil	Flash point temperature [°C]	Trend towards oil without additive
Base oil	201.3 ±0.57	
Base oil + shungite	201.3 ±0.57	—
Base oil + carbon nanotubes	199.2 ±0.57	↓
Base oil + fullerens C_{60}	204.2 ±0.57	↑

Table 3. The values of the ignition temperature of the mixture prepared at the Marinol RG1240 oil
Tabela 3. Wartości temperatury zapłonu dla mieszanin na bazie oleju Marinol RG1240

Tested oil	Flash point temperature [°C]	Trend towards oil without additive
RG1240	232.2 ±0.57	
RG1240 + shungite	231.3 ±0.57	—
RG1240 + carbon nanotubes	229.2 ±0.57	↓
RG1240 + fullerens C_{60}	236.2 ±0.57	↑

The flash point values obtained in the measurements are lower than the values in the oil characteristics due to the different measurement method used **[L. 27, 28]**. This difference is about 30°C and is typical for the differences resulting from comparing the results obtained with the open cup method (manufacturer's data) and the closed cup method (our own results).

A slight influence of nano-additives on the change of the flash point value in relation to both unmodified oils was observed. It can be concluded that the addition of shungite did not actually change these temperature values. On the other hand, oils with the addition of carbon nanotubes showed a minimally lowered (by approx. 2–3°C) value of the flash point, both in the case of base oil and Marinol oil. The greatest, but still relatively small, effect on the change of this parameter was shown by the addition of C_{60} fullerenes as an oil modifier. Under the influence of this additive, the flash point value increased by 3°C for the mixture with the base oil and 4°C for the mixture based on Marinol oil **[L. 23]**.

The obtained results differ slightly from the results quoted in the literature analysis. While the tendency of change resulting from modification with fullerenes has been confirmed, its value is significantly lower. On the other hand, in the case of oil modification with carbon nanotubes, both the trend and the change gradient were not confirmed. The flash point results for the shungite modification can be considered confirmed. Obviously, the differences may result from reasons attributable to the different base oils tested, although it is characteristic that the nature and similar values of the change were obtained for both base oil and lubricating oil mixtures. From the utility point of view, it is important that none of the nanomodifiers has a significant negative effect on the values of this parameter, and in the case of the addition of fullerenes, it can be concluded that the effect is positive.

The next research carried out concerned the rheological properties of the prepared mixtures. As already indicated in the theoretical part of the work, these properties are largely responsible for the lubrication conditions in friction nodes, in particular, in the conditions of liquid friction. As part of these studies, the characteristics of changes in oil viscosity as a function of temperature and as a function of shear rate were obtained.

The first of them were carried out in the range of temperature changes from 10°C to 90°C in the 5°C step mode at a constant shear rate of 1000 s^{-1}. Such a measurement mode ensured a sufficiently long time of thermal oil stabilization, which allowed avoiding the effect of shifting the obtained values resulting from transient thermal conditions in the measurement system. The obtained results, averaged from three measurement series for each tested oil composition, are presented in **Fig. 1** and **Fig. 2** for mixtures with base oil and those based on Marinol RG 1240 oil, respectively.

Differences in the characteristics of the starting oils and their modified versions differ only to a slight extent. In addition, **Table 4** and **Table 5** provide the determined values of the dynamic viscosity coefficient at several characteristic temperatures.

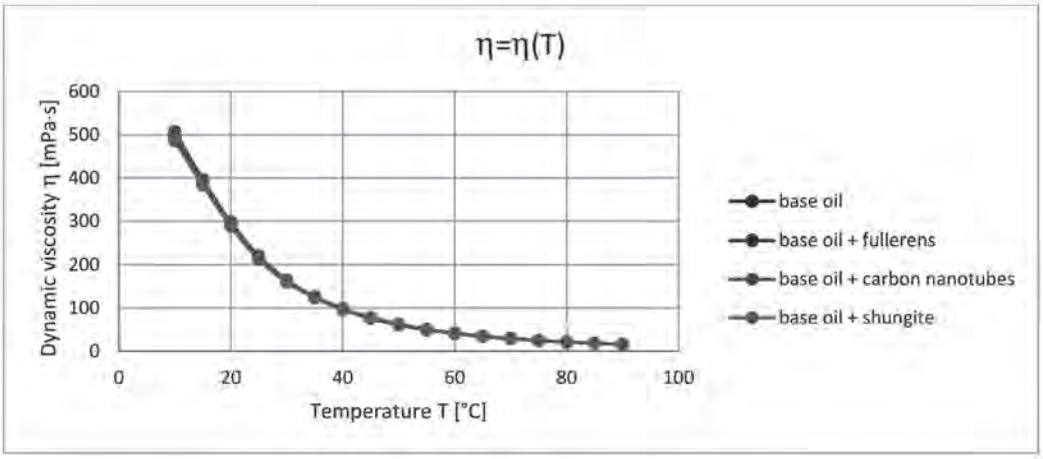


Fig. 1. Characteristics of dynamic viscosity changes of base oil and its modified mixtures as a function of temperature η = η(T)

Rys. 1. Charakterystyki zmian lepkości dynamicznej oleju bazowego i jego zmodyfikowanych mieszanin w funkcji temperatury η = η(T)

The main conclusion that emerges from the analysis of the results obtained in these studies is the lack of a significant influence of the tested carbon nanoadditives on the values of the viscosity coefficient. Among the three tested nanoadditives, only the oils modified with carbon nanotubes showed slightly higher values of changes, but they also did not exceed the level of 2–3% of relative differences in the obtained values. Comparable results of changes in the value of the dynamic viscosity coefficient were obtained for both groups of oils.

Table 4. Values of the dynamic viscosity coefficient for the modified base oil
Table 4. Wartości dynamicznego współczynnika lepkości dla modyfikowanego oleju bazowego

	Temperature [°C]				Relative average change in value [%]
	20°C	**40°C**	**70°C**	**90°C**	
Base oil	290.94	96.06	24.50	12.67	–
Base oil + shungite	288.26	96.18	24.81	12.83	+ 0.94
Base oil + carbon nanotubes	296.62	99.01	25.78	13.45	+ 3.12
Base oil + fullerens C_{60}	289.39	96.22	24.71	12.73	+ 0.96

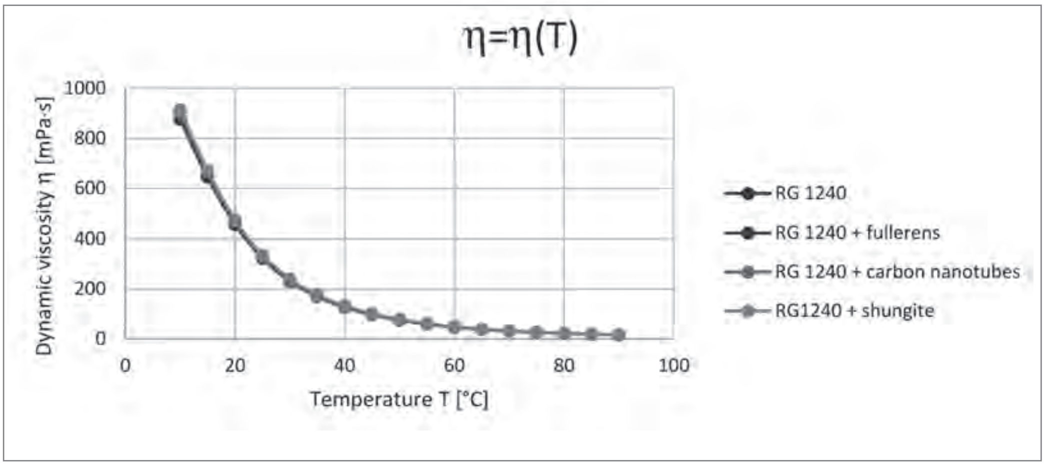
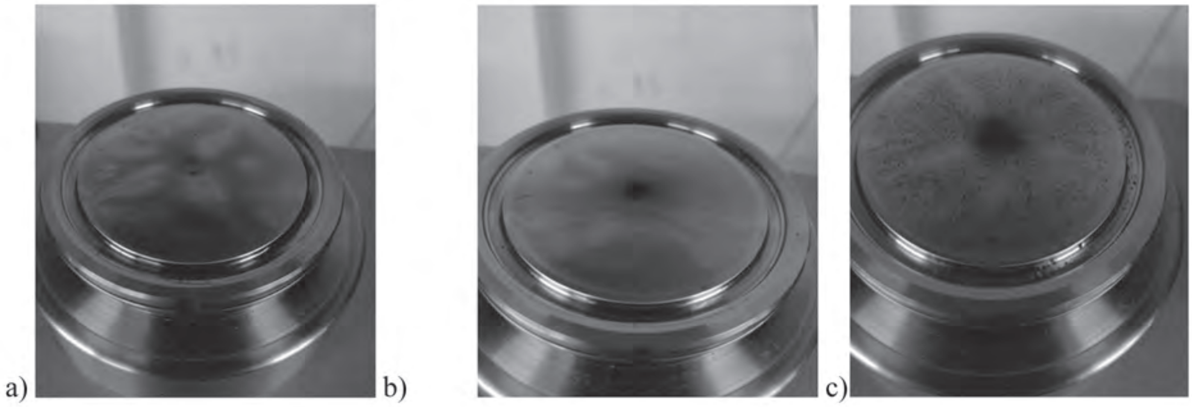


Fig. 2. Characteristics of dynamic viscosity changes of Marinl RG1240 oil and its modified mixtures as a function of temperature η = η(T)
Rys. 2. Charakterystyki zmian lepkości dynamicznej oleju morskiego Marinol RG 1240 i jego zmodyfikowanych mieszanin w funkcji temperatury η = η(T)

Table 5. Values of the dynamic viscosity coefficient for the modified Marinol RG1240 oil
Tabela 5. Wartości dynamicznego współczynnika lepkości dla modyfikowanego oleju Marinol RG 1240

	Temperature [°C]				Relative average change in value [%]
	20°C	**40°C**	**70°C**	**90°C**	
RG1240	458.66	126.95	31.49	15.80	–
RG1240 + shungite	473.81	131.00	32.34	16.38	+ 1.34
RG1240 + carbon nanotubes	474.71	131.95	32.44	16.42	+ 1.39
RG1240 + fullerens C_{60}	461.16	127.88	31.68	15.91	+ 0.86

Interesting observations were made during the research on changes in viscosity as a function of temperature. Depending on the nanoadditives used as oil modifiers, their distributions on the flat plate of the rheometer measurement system differed significantly at the end of the study, despite the fact that, before the measurement, all of them were homogeneous, well-mixed suspensions. Only in the case of the suspension with fullerenes, the test mode did not substantially affect the distribution of particles in the oil sample. In the case of the shungite sample, large amounts of carbon particles accumulated in the centre of the plate. A similar effect could be observed for samples with carbon nanotubes, and additionally, nanotube particles remaining in the oil volume formed larger aggregated structures. The above observations are illustrated in **Fig. 3**.



Rys. 3. Rozkład cząsteczek nanomodyfikatorów na płytce reometru zaobserwowany po badaniu zmian lepkości w funkcji temperatury dla próbki: a) olej + fullereny, b) olej + szungit, c) olej + nanorurki

Fig. 3. Distribution of nanomodifier molecules on the rheometer plate observed after the study of viscosity changes as a function of temperature for: a) oil + fullerens, b) oil + shungite, c) oil + carbon nanotubes

The rheological research was supplemented by determining the characteristics of changes in oil viscosity as a function of shear rate $\eta = \eta(\gamma)$. These tests were carried out under the conditions of a constant temperature of 80°C and the shear rate increased linearly from 0 up to the value of 100,000 s^{-1}.

The obtained characteristics indicate that the addition of carbon nanomodifiers to oils, regardless of their allotropic forms, does not change the nature of the course of viscosity changes in relation to base oils, and these waveforms are very similar. This observation applies to both the mixtures prepared on the base oil and on the Marinol. Due to the small variability of the value of the dynamic viscosity coefficient with the shear rate, it can be concluded that all these oils, basic and modified, exhibit almost Newtonian properties. What is noteworthy, adding each of the nanomodifiers to Marinol RG 1240 oil slightly increased (by approx. 0.5 mPa·s) its viscosity. Such an effect was not observed in the case of mixtures based on base oil. The obtained curves of the aforementioned characteristics of viscosity changes as a function of shear rate are presented in **Fig. 4** and **Fig. 5**.

The last stage of the experimental tests was the examination of the lubricating properties of modified oils. These tests were carried out on a four-ball head tester T-02U according to our own research plan. The main part of the test lasted 2700 s at the condition of a constant load of 300 N and a constant rotational speed of the spindle of 1000 min^{-1}. Such selected test conditions allowed us to ensure heat exchange conditions similar to the established ones and the related relatively low oil temperature change during the test, ranging from 48°C to 54°C. To ensure the same, repeatable test conditions, 10-milliliter oil samples (constant volume) were subjected to initial preparation, which included the run-in process for 900 s under a load of 450 N and a spindle speed of 1450 min^{-1}. During this time, the samples obtained the required constant test start temperature. The obtained results are presented in **Fig. 6** and **Fig. 7** for the modified base oil and the modified Marinol RG 1240 oil, respectively.

The obtained results show significant differences in the obtained values of the friction coefficients (f) depending on the allotropic form of the modifier used. Oils modified with fullerene C_{60} showed the most favourable effect on friction conditions. The value of the coefficient of friction significantly decreased both in relation to the base oil and RG1240 lubricating oil. In both cases, the

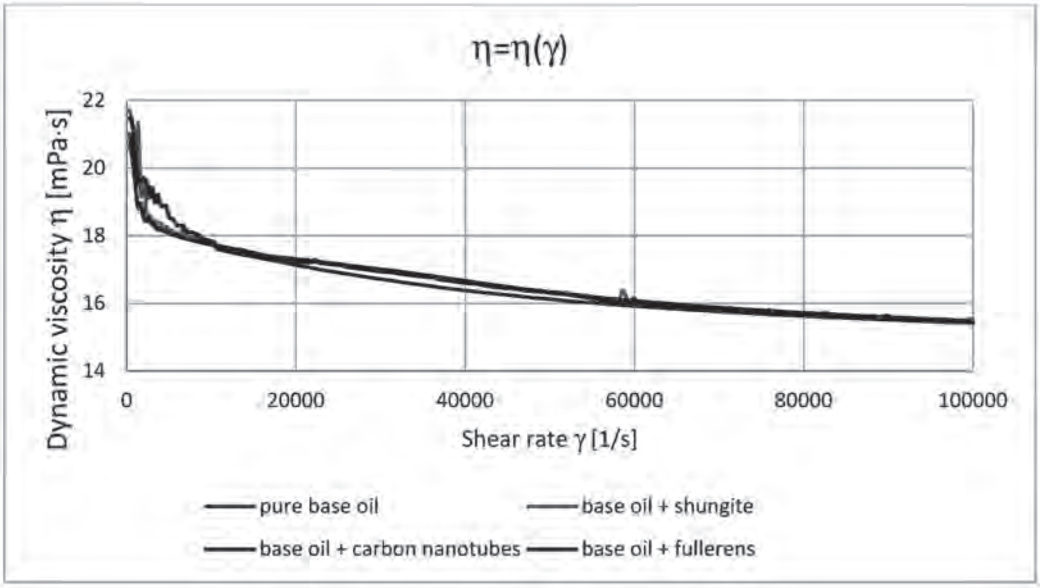


Fig. 4. Characteristics of dynamic viscosity changes of base oil and its modified mixtures as a function of shear rate η = η(γ)

Rys. 4. Charakterystyki zmian lepkości dynamicznej oleju bazowego i jego zmodyfikowanych mieszanin w funkcji szybkości ścinania η = η(γ)

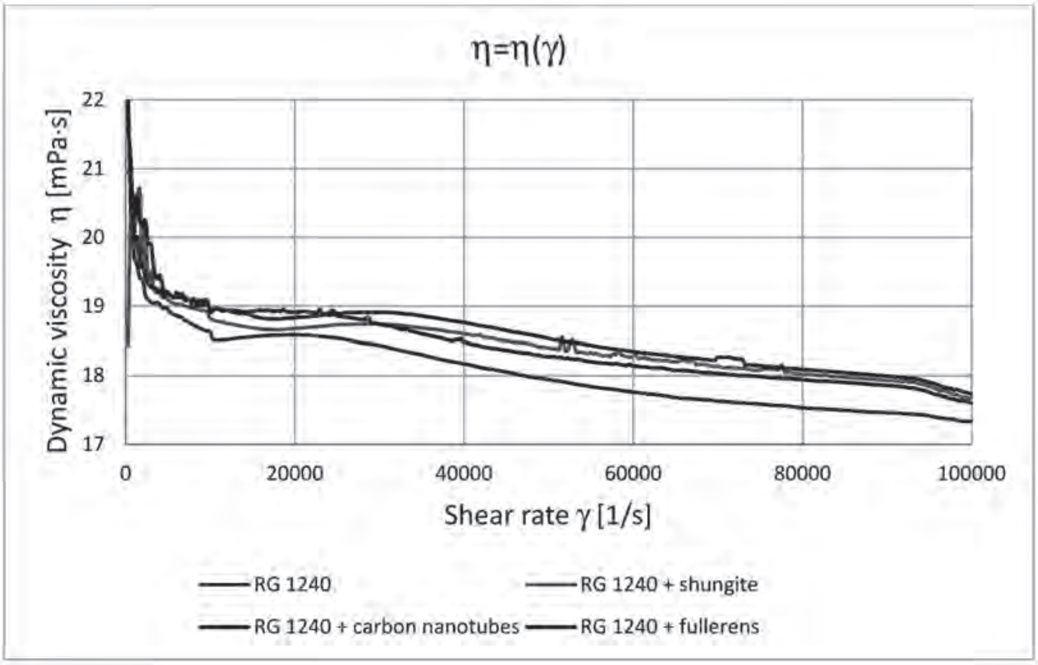


Fig. 5. Characteristics of dynamic viscosity changes of Marinol RG1240 oil and its modified mixtures as a function of shear rate η = η(γ)

Rys. 5. Charakterystyki zmian lepkości dynamicznej oleju Marinol RG 1240 i jego zmodyfikowanych mieszanin w funkcji szybkości ścinania η = η(γ)

obtained advantageous difference in the coefficient value was approx. Δf = 0.05. Shungite modified oils were also characterized by slightly lower values of the determined coefficient. However, in this case, the change was significantly smaller and did not exceed Δf = 0.02. Modifying oils with carbon nanotubes had almost no effect on the determined parameter. In this case, the obtained

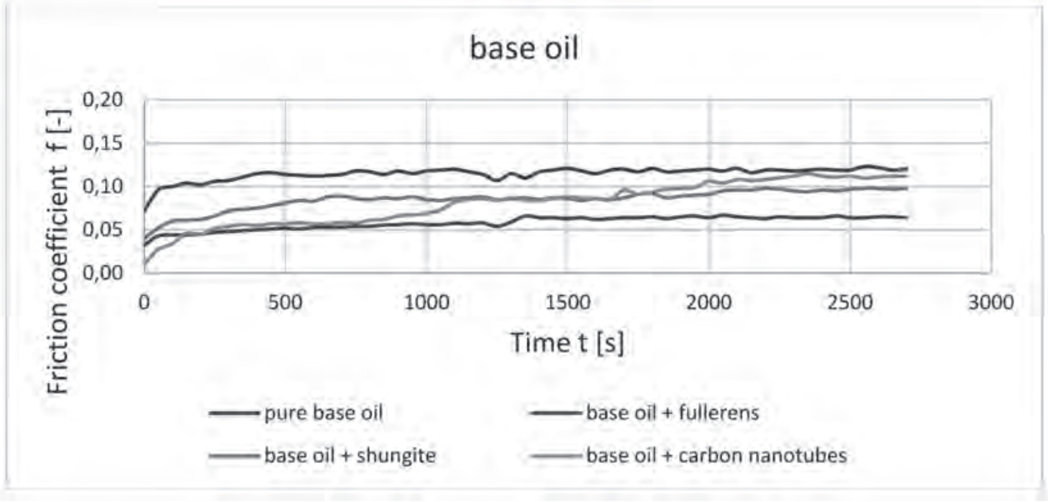


Fig. 6. Values of friction coefficients for modified base oils
Rys. 6. Wartości współczynników tarcia dla zmodyfikowanych olejów bazowych

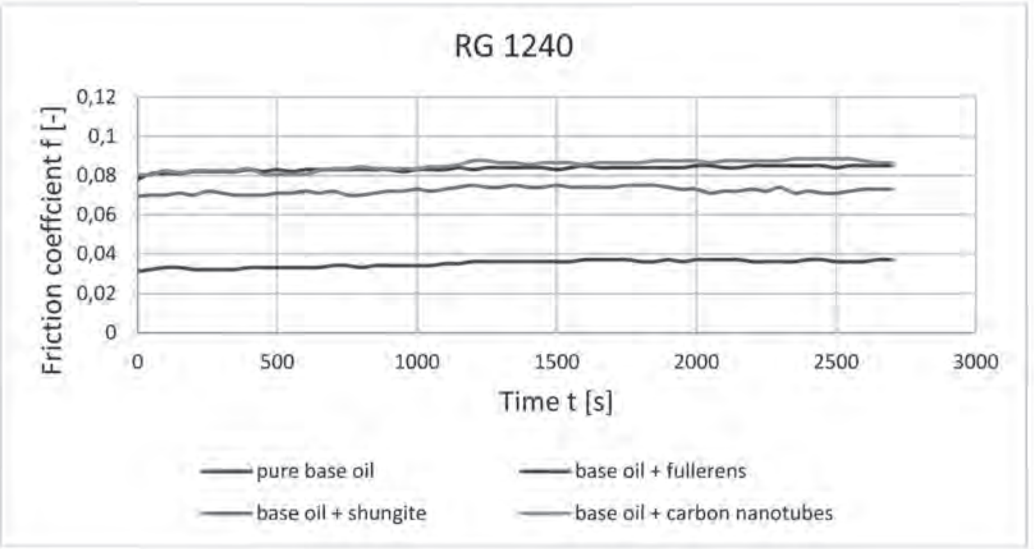


Fig. 7. Values of friction coefficients for modified RG1240 oils
Rys. 7. Wartości współczynników tarcia dla zmodyfikowanych olejów smarnych RG1240

values corresponded to the values characteristic for unmodified oils. Such a weak effect is probably due to the shape and size of these molecules as well as their chemical neutrality, which would be confirmed by the conclusions that can be found in **[L. 7]**. Another suggested reason may be the exceptional susceptibility of the solution with nanotubes to sedimentation, particle aggregation, and phase separation observed in other studies. It is characteristic and somewhat surprising that the obtained changes in the values of the friction coefficients did not depend on the type of oil used as the base at all. Accompanying the observation made during this study was the fact that the nanomodifiers additionally showed anti-seize properties. When testing pure base oil, the ball arrangement seized twice. Such an event did not take place during any of the tests of this oil after its modification with nanoadditives. The course of the test in which the seizure phenomenon took place was not presented in **Fig. 7** due to the disproportion between the typical values of the friction coefficient and those that accompanied this exceptional test course, where the friction coefficient reached values up to f = 0.46.

The tests on the four-ball apparatus were supplemented with the measurements of the diameter of the wear marks that remained on the balls after the test. For this purpose, a SmartZoom 5 measuring microscope with software enabling the measurement of selected geometric quantities was used. The results of the diameter measurements are presented in **Table 6**.

In all cases, the use of nanomodifiers resulted in a reduction in the diameter of the scuff mark visible on the balls. This also applied to spheres after testing with the use of carbon nanotubes, despite the fact that the previously determined coefficients of friction did not differ from those obtained for unmodified oils. The largest difference in the trace diameter value concerned modification with fullerenes, and the smallest with carbon nanotubes.

Table 6. Mean values for traces of seizure modified oils with taking into account the standard deviation σ
Tabela 6. Uśrednione wartości śladów zatarcia dla olejów z uwzględnieniem odchylenia standardowego σ

	Mean values for traces of seizure [mm]	
	Base oil	**Marinol RG 1240**
Pure oil	0.722 ±0.006	0.435 ±0.006
Oil + fullerens C_{60}	0.483 ±0.005	0.344 ±0.004
Oil + shungite	0.515 ±0.005	0.376 ±0.003
Oil + carbon nanotubes	0.530 ±0.006	0.402 ±0.004

SUMMARY

The tests of selected physicochemical properties of oils and the analysis of the obtained results confirm that the use of carbon nanomodifiers could positively affect the operating conditions in tribomechanical nodes of marine engines and other power plant equipment lubricated with such improved mineral oils and affect their efficiency, reliability, and durability. In view of the obtained results, the most advantageous impact in terms of operation would be the modification of oils with C_{60} fullerene particles. On the other hand, it is currently the most expensive of the nanoadditives used and finally the economic balance may effectively prevent the utilitarian use of such oils in practice. The advantage of these nanomodifiers is probably due to the fact that even trace amounts of such an additive can significantly change the anti-wear properties of lubricating oils.

An alternative solution in the context of the obtained results could be the use of much cheaper shungite as a modifier. However, in this case, changes in key tribological properties are much less effective than in the case of fullerenes. It should also be taken into account that, in the natural state, it is virtually impossible to obtain the purest type of this type I coal, and the effectiveness of varieties that are worse in this respect could offset the overall favourable balance.

Simple, direct use of carbon nanotubes as modifiers would not bring the expected benefits at present. It is possible that the effective use of this nano-modifier would require the presence of an additional surfactant in the oil composition to counteract both aggregation and sedimentation of the carbon particles.

REFERENCES

1. Sulzer: Instrukcja techniczno-ruchowa silników Sulzer typu RND, 2020.
2. Ginzburg B.M., Shibaev L.A., Kireenko O.F., Shepelevskii M.V., Baidakov M.V., Sitniakova A.A.: Antiwear effect of fullerene C_{60} additives to lubricant oils, "Russian Journal of Applied Chemistry" 2002, Vol. 75, No. 8, pp. 1330–1335.
3. Huang H.D., Tu J.P., Gan L.P., Li C.Z.: An investigation on tribological properties of graphite nanosheets as oil additive, "Wear" 2006, Vol. 261, pp. 140–144.
4. Kwangho L., Yujin H., Seongir Ch., Youngmin Ch., Laeun K., Soo-Hyung K.: Understanding the Role of Nanoparticles in Nano-oil Lubrication, "Tribology Letters" 2009, Vol. 35, pp. 127–131.
5. Rapoport L., Leshchinsky V., Lvovsky M., Volovik Y., Tenne R.: Mechanism of friction of fullerenes, "Ind. Lubr Tribology", Vol. 54, 2002, pp. 171–176.
6. Wu Y.Y., Tsui W.C., Liu T.C.: Experimental analysis of tribological properties of lubricating oils with nanoparticle additives, "Wear" 2007, Vol. 262, pp. 819–825.
7. Yujin H., Changgun L., Seongir Ch., Doohyun K., Kwangho L., Jaekeun L., Soo H.K.: Effect of the size and morphology of particles dispersed in nano-oil on friction performance between rotating discs, "Journal of Mechanical Science and Technology" 2011, Vol. 25 (11), pp. 2853–2857.
8. Kogovsek J., Kalin M.: Various MoS_2-, WS_2- and C-Based Micro- and Nanoparticles in Boundary Lubrication, "Tribology Letters" 2014, Vol. 53, pp. 585–597.
9. Voronin S.V., Suranov A.V., Suranov A.A.: The Effect of Carbon Nanoadditives on the Tribological Properties of Industrial Oils, "Journal of Friction and Wear" 2017, Vol. 38, No. 5, pp. 359–363.
10. Jaekeun L., Sangwon Ch., Yujin H.: Enhancement of Lubrication Properties of Nano-oil by Controlling the Amount of Fullerene Nanoparticle Additives, "Tribology Letters" 2007, Vol. 28, pp. 203–208.
11. Tochilnikova D.G., Kupchin A.N., Lyashkov A.I., Ponyaev S.A., Shepelevskii A.A., Ginzburg B.M.: Effect of Fullerene Black Additives on Boundary Sliding Friction of Steel Counterbodies Lubricated with Mineral Oil, "Journal of Friction and Wear" 2012, Vol. 33, No. 2, pp. 94–100.
12. Lomanyevaa S., Ulyanova A., Eremina M.A., Tarasov V.V., Lys V.F.: Interaction mechanisms between Schungite and friction surfaces under High-energy Ball Milling, "Journal of Friction and Wear" 2018, Vol. 39, No. 4, pp. 319–325.
13. Tupotilov N., Ostrikov V.V., Kornev A.Yu.: Finely disperse minerals as antiwear additives for lube oils, "Chemistry and Technology of Fuels and Oils" 2008, Vol. 44, No. 1, pp. 29–33.
14. Ахматов А.С.: Молекулярная физика граничного трения, ФИЗМАТГИЗ, 1963, с. 472.
15. Chinas-Castillo F., Spikes H.A.: Mechanism of action of colloidal solid dispersions, "Journal of Tribology" 2003, Vol. 125, pp. 152–158.
16. Hu Z.S., Lai R., Lou F., Wang L.G., Chen Z.L., Chen G.X., Dong J.X.: Preparation and tribological properties of nanometer magnesium borate as lubricating oil additive, "Wear" 2002, Vol. 252, pp. 370–374.
17. Zhou J., Yang J., Zhang Z., Liu W., Xue Q.: Study on the structure and tribological properties of surface-modified Cu nanoparticles, "Materials Research Bulletin" 1999 , Vol. 34 (9), pp.1361–1367.
18. Liu G., Li X., Qin B., Xing D., Guo Y., Fan R.: Investigation of the mending effect and mechanism of copper nano-particles on a tribologically stressed surface, "Tribology Letters" 2004, Vol. 17 (4), pp. 961–966.
19. Tao X., Jiazheng Z., Kang X.: The ball-bearing effect of diamond nanoparticles as an oil additive, "Journal of Physics D: Applied Physsics" 1996, Vol. 29 (11), pp. 2932–2937.
20. Greenberg R., Halperin G., Etsion I., Tenne R.: The effect of WS_2 nanoparticles on friction reduction in various lubrication regimes, "Tribology Letters" 2004, Vol. 17 (2), pp. 179–186.
21. Rabaso P., Ville F., Dassenoy F., Diaby M., Afanasiev P., Cavoret J., Vacher B., Le Mogne T.: Boundary lubrication: Influence of the size and structure of inorganic fullerene-like MoS2nanoparticles on friction and wear reduction, "Wear" 2014, Vol. 320, pp. 161–178.
22. Huang H.D.,Tu J., Zou T.Z., Zhang, L.L.: Friction and wear properties of IF-MoS_2 as additive in paraffin oil, "Tribology Letters" 2005, Vol. 20 (3), pp. 247–250.

23. Ehsanoo-Ilah E., Rashidi A., Ahmadi H., Mahnaz P.: Thermal and rheological properties of oil-based nanofluids from different carbon nanostructures, “International Comunications in Heat and Mass Transfer” 2013, Vol. 48, pp. 178–182.
24. Bon-Cheol H., Young-Chul H., Jung-Eun L., Sang-Ho P.: Tribological effects of fullerene (C60) nanoparticles added in mineral lubricants according to its viscosity, “International Journal of Precision Engineering and Manufacturing” 2010, Vol. 10, pp. 607–611.
25. Moshkovith A., Perfiliev V., Verdyan A., Lapsker I., Popovitz-Biro R., Tenne R., Rapoport L.: Sedimentation of IF-WS_2 aggregates and a reproducibility of the tribological data, “Tribology International” 2007, Vol. 40, pp. 117–124.
26. Chen Y., Renner P., Liang H.: Dispersion of Nanoparticles in Lubricating Oil: A Critical Review, “Lubricants” 2019, Vol. 1, pp. 1–21.
27. http://lotosoil.pl/resource/show/17660.pdf.
28. https://www.lotos.pl/321/p,367,c,83/dla_biznesu/oleje/oleje_bazowe/olej_bazowy_sae_10/95.