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Experimental Wear Analysis of Nano-Sized Titania Particles as Additives in Automotive Lubricants

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Abstract: This study focuses on the wear effects of nano-sized titania as a potential engine lubricant additive. Titanium dioxide nanoparticles have promising wear-reducing properties and significant tribological potential. In this article, titania nanoparticles were homogenized in Group III automotive oil at five different concentrations (0.1; 0.2 . . . 0.5 wt%). The nanodoped oil samples were tested on a linear oscillating tribometer with oil circulation. Based on the tribological results, titania nanoparticles increased friction by 20–32% but can reduce the wear area by up to 32%. According to the confocal microscopic examination, wear volume can be reduced by up to 57% with titania nanoparticles. Titania nanoparticles improved the repeatability of tribological measurements. A scanning electron microscopy examination of the wear track revealed that the characteristic wear of the tribological system was abrasive, but a significant amount of adhesive wear was also observed. Energy dispersive X-ray spectroscopy analysis found that the nanoparticles fill the deeper trenches of the wear. The worn surface uniformly contains TiO_2 particles and the quantified normalized titanium concentration was between 0.56 and 0.62%.

Keywords: tribology; titanium dioxide; nanoparticle; wear; friction; adhesion; abrasion

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1. Introduction

The modern vehicle industry consumes a lot of energy and resources for the production of automotive parts. Examining the entire life cycle of the parts, it can be concluded that it pays off in the long term if the wear properties of the parts are improved. An automotive part with a longer service lifespan means a less frequent replacement period, which in turn requires fewer spare parts. In this way, the emission and environmental impact resulting from the production, transportation and storage of components can be reduced indirectly. Among the nanoparticles, many can significantly reduce the amount of wear—these include oxide ceramics such as titanium dioxide. The oxide nanomaterials are materials with ceramic properties, strong chemical passivity and good mechanical characteristics, which have already been proven in numerous studies to be good friction-reducing and excellent wear-reducing lubricant additives to be used in the future. This article focuses on titania nano-additives and their anti-wear effect to prove their function.

2. Literature Review

The use of nanoparticles as a lubricant additive in the automotive industry has already been covered by numerous studies that examine their effect as a function of tribological performance, depending on the tribological system, their material, their morphology, their size and their thermophysical properties [1].

Rajaganapathy et al. reported the friction and wear-decreasing effect of nano-sized titania particles by using them as lubricant additives in palm and brassica oil during pin-on-disc tribometer tests [2]. The studies report improvements in mechanical efficiency by decreasing the coefficient of friction (COF) and heat losses, which led to the usage of nanoparticles in the grease and/or liquid lubrication [3]. To prepare the additive, several methods are used such as stearic acid, which is used to prepare high purity TiO_2 with a 40 nm diameter [4].

Many researchers enhance nanoparticles through surface modification. Using tetrafluorobenzoic -acid is also a preparation method for much smaller partials (10 nm); employing this method, the lubricant is tested and characterized to reduce the wear and friction for mechanical parts under high pressure [5]. Other methods are used as well, such as oleic acid (OA) and lanthanum, prepared by sol-gel. This method remarkably improved the anti-wear properties in the sliding steel surfaces [6]. Harshvardhan et al. also improved the dispersion of titania nanoparticles using oleic acid as a surfactant. In the research, SN-500 (solvent-neutral) base oil was doped with titania nanoparticles, and the resulting mixture was tested at three different loads. Based on their results, they found that by using titanium nanoparticles in concentrations of 0.5 wt% and 0.75 wt%, friction can be reduced by 21–85%, while wear can be reduced by 25–50% [7]. The nanoparticles preparation method is not the only factor that affects heat absorption. The concentrations of the nanoparticles and the density and the size of the nanoparticles factor in the results. Having a small concentration, such as 0.01 wt% of TiO_2, results in reducing the wear scaring up to 20% [8]. In addition, adding nanoparticles has an almost 32% positive effect more than base lubricant [9]. However, maintaining the size and the density at as small a size as possible works to our advantage by not only decreasing the coefficient of friction (COF) [10,11] but also stabilizing it to reach the minimum value of COF (0.006). By using 1% TiO_2 nanoparticles, the lifespan, compared with commercial lubricants, can be increased [12,13].

TiO_2 nanoparticles showed a 49.5% COF reduction and a 97.5% wear scar reduction in four-ball tests under dry conditions and by using a water solution, respectively [14]. Replacing the water-based lubricants with oil will work to improve the results, using a reciprocating sliding tribology tester; cupric oxide with a base oil lubricant has a reduction percentage of 5.8% for COF and 78.8% for wear scar depth. Meanwhile, an API-SF lubricant with a CuO nanoadditive will result in reducing the COF by 18.4% and the wear scar depth by 16.7% [15]. Using rice bran oil and adding cerium dioxide (CeO_2), titanium dioxide (TiO_2) and zirconium dioxide (ZrO_2) will vary the concentration of each nanoparticle between 0.1 and 1 wt%. At 0.7 wt%, ZrO_2 showed the minimum COF and wear scar diameter (WSD), which was the highest needed concentration. Meanwhile, 0.5 wt% CeO_2 showed the maximum amount of COF reduction and an 8% wear-scar diameter reduction. However, the TiO_2 showed tribological proprieties at 0.3 wt%, which made it the least concentration needed, and by increasing the concentration, the tribological proprieties increased. The best concentration for TiO_2 was 0.8 wt% [3,16,17]. Hamisa et al. used a titania and silica nanoparticle hybrid in a polyol-ester-based lubricant. The stability of the oil sample was confirmed through a zeta potential measurement and visually. The stable oil sample provided a suitable basis for reducing friction by up to 37.5% and wear by up to 26.4% [18]. Ismail et al. reached similar results when they performed measurements using PVE-modified lubricant as a base [19]. As mentioned earlier, the nanoparticles tend to improve grease lubricants, and the benzoic acid/stearic acid titanium complex and the sebacic acid/stearic acid titanium complex were doped with TiO_2 and SiO_3. Compared with nanoparticles-free grease, TiO_2 with benzoic/stearic acid reduced the COF by 22.97% and reduced the WSD by 4.35%. TiO_2 with Sebacic/stearic acid reduced the COF by 35.98% and the WSD was reduced by 8.95%. SiO_3 with a benzoic/stearic acid titanium complex reduced both the COF and the wear scar diameter by 24.47% and 1.8%, respectively. However, SiO_3 with a sebacic/stearic acid titanium complex reduced the COF and the WSD by 29.58% and 4.55%, respectively [20]. Kuo et al. also used titania to improve the tribological properties of greases. During their tests, they compared the effect of micro- and nano-sized titania particles (contact resistance, friction, wear) on a laser-textured surface. A synergistic effect was established due to the laser-structured surface, which was capable of carrying the lubricant and collecting wear debris, therefore helping the particles to act in the tribosystem [21]. Regardless, to reduce the WSD by 0.65 mm, 11% of the nano-sized TiO_2 and 6.1% of the micro-TiO_2 are needed. However, micro-TiO_2 reduces the COF by 6.9%; meanwhile, nano-TiO_2 reduces the COF by 15.2% and this variation in results happens due to the spherical shape of the titania nanoparticles [22]. The spherical shape of the TiO_2 nanoparticles acts as nanobearing between the sliding surfaces, which reduces the friction. Moreover, the nanoparticles fill the wear valleys in the surfaces, which was shown to reduce the scaring up to 80.84%, filling the scar [23]. It also factors in the COF reduction by creating a tribofilm containing the nanoparticles [24–26]. Sharma et al. investigated the combined effect of zinc dialkyldithiophosphate and titania and focused on tribofilm formation. It was found that they are excellent additives individually, but when they are used together, an adequate tribofilm does not form and the wear increases. They also presented a method in which the surface of the titania nanoparticles is modified with boron atoms using plasma functionalization—this helped to improve the tribofilm formation [27]. When CeO_2 and TiO_2 are combined in the lubricant, less TiO_2 is required to achieve the intended results [28].

Some researchers have already investigated nanoparticles as engine oil additives when measuring internal combustion engines. When using nanographite below 50 nm, engine performance increased, and fuel consumption and emissions decreased [29]. In a full stroke in the internal combustion engine, when the lubricant contained only a concentration of 1.75 wt% oleic acids, the COF is slightly reduced mainly due to the chemical reaction. When adding Al_2O_3 to the lubricant and measuring the COF at the top dead centre and the bottom dead centre, the COF is lower by 35%, and the wear scar on both the piston ring and cylinder liner is 30–33% less than when using an engine lubricant without nanoadditives. However, in the case of using nano-sized TiO_2, then the COF reduction is 51% and the wear scar is reduced by 16–18% [3,16,30]. Theoretically, by using the Reynolds equation, it is possible to estimate the pressure and load-carrying capacity for TiO_2 concentration. Having TiO_2 in the lubricant even with a small concentration (0.001 v/v%) increases the load-carrying capacity by 40% more compared with the reference lubricant (without TiO_2) [14]. The increase of (0.0015 TiO_2 volume fraction) in the particle packing fraction from 7.77 to 10 leads to an increase in the load-carrying capacity by up to 35%. Realistically, the simulation of the accurate shear viscosity is possible using the Krieger–Dougherty viscosity model [31]. Mubashar et al. investigated the rotational and sliding properties of hybrid nanofluid-based engine oils with other substances using a numerical method [32].

The concentration effect of the nano-sized TiO_2 additive was studied and the results were established. Pan et al. investigated the lubrication conditions of a lubricant film containing titania nano-additives used for micro deep drawing. Using the glycerine-based nanolubricant, the pulling force could be reduced by up to 36.6%. They also found that too much nano-additive (~4 wt%) already creates a significant number of agglomerations in the lubricant, which hurts the performance of tribological systems [33]. It is important to study the effect of nano-sized TiO_2 under different loads. When applying different loads (40, 80, 120 and 160 kg) for 10 min at 1200 rpm, the TiO_2 reduced the COF by 15% and the WSD by 11%. Meanwhile, when the load was minimum, the TiO_2 worked as a protective layer [34]. Maintaining a 4 kg load, 0.3 wt% TiO_2 reduced the COF of aluminum alloy metals by 86.48% [35]. Ilie et al. investigated titanium dioxide as a solid lubricant. A control volume fractional coverage theoretical model was prepared for the tests. Their results established the surface self-healing ability of titania nanopowder. The results of the theoretical model and the actual measurement were promisingly close to each other [13]. Based on the scientific literature, the tribological functioning mechanism of titania nano-additive is not yet fully known. The aim is to support knowledge about the operating anti-wear mechanism with the measurement results.

3. Materials and Methods

Titanium dioxide (TiO_2, also named titania) is the crystalline oxide of titanium transition metal. Titanium dioxide, used for tribological tests, was purchased from Alfa Aesar

GmbH, Karlsruhe, Germany. The titanium dioxide (99.9% purity) appeared in the form of a white APS powder, which contains spherical particles with a size of less than 32 nm diameter. The titanium dioxide used had an anatase crystal structure, which is the most brittle and least hard form occurring in nature. Titania nanoparticles have a hardness of ~800 HV (due to their high hardness, they can also be used as cutting fluid additives [36]), a density of ~3890 kg/m^3, a Young's modulus of ~157 GPa and a high chemical and corrosion resistance [37–39]. Titania nanoparticles are one of the most common materials used in nanotechnology, and therefore the environmental exposure of this particle is one of the largest. Numerous studies examine its long-term effects on living organisms (toxicity, carcinogenicity, etc.), the results of which are divisive, so titania nanoparticles must be used with due caution (for example, as an additive in closed tribological systems).

Before mixing the titania nanoparticles into the lubricant, they were examined with a scanning electron microscope (SEM). Based on visual observation, titania is a white powder. To make sure that the manufacturer provided titania nanopowder, it was examined using energy dispersive X-ray spectroscopy (EDX). EDX cannot detect impurities, but it is suitable for identifying the material (see Figure 1). Based on the EDX spectrum, it was established that the examined nanopowder was titanium dioxide. The high carbon peak came from the glue needed to hold the powder during the measurement.

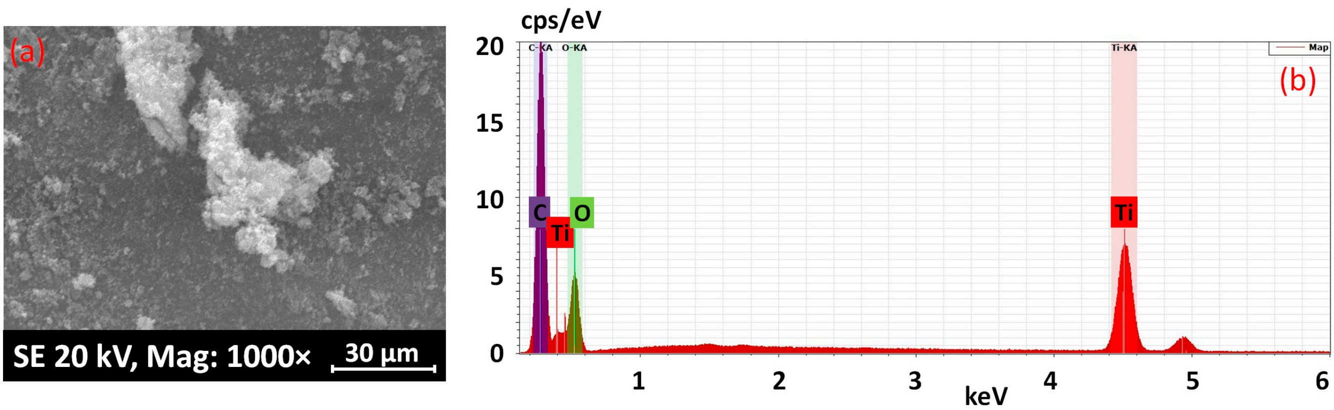

Figure 1. Scanning electron micrograph of titanium dioxide nanoparticles with 1000× magnitude, shown on the (**a**). The EDX spectrum of the nanoparticles is shown on the (**b**).

A refined mineral base oil of Group III type, with a viscosity of 4 cSt, used here for the measurements, is the basis of most commercially available engine lubricants. The base oil used for the tribological tests was provided by MOL-LUB Kft., Almásfüzitő, Hungary. The base oil produced by MOL consists of a mixture of C20-C50 hydrocarbons (CAS 64742-54-7; CAS 72623-87-1). The base oil does not contain any additives, titanium-containing components or components that could chemically react with the titania nano-additive.

The oil samples used for the tribology tests were determined based on the concentrations most often recommended in the scientific literature: 0.1 wt%; 0.2 wt% and 0.3 wt%, with 0.4 wt% and 0.5 wt% titanium dioxide content. The amount of nanopowder required for the mixtures was measured in a beaker placed on a microbalance. Enough base oil was then added to achieve the desired concentration. After that, the oil sample containing nanopowder was placed on a magnetic stirrer for 5 min at 1000 rpm. The magnetic stirrer began to separate the large clump of nanopowder into smaller clumps and distribute them evenly throughout the beaker. The oil sample was then placed directly in an ultrasonic bath at a temperature of 50 °C for 30 min. Using high-frequency sound waves, the ultrasonic bath broke the secondary bonds between the individual nanoparticles, thereby creating a homogeneous monodispersion in the lubricating oil. The oil sample prepared in this way was ready for tribological tests and was placed on a magnetic stirrer at 800 rpm until its use. Figure 2 represents the used magnetic stirrer and an example of the prepared nanolubricants.

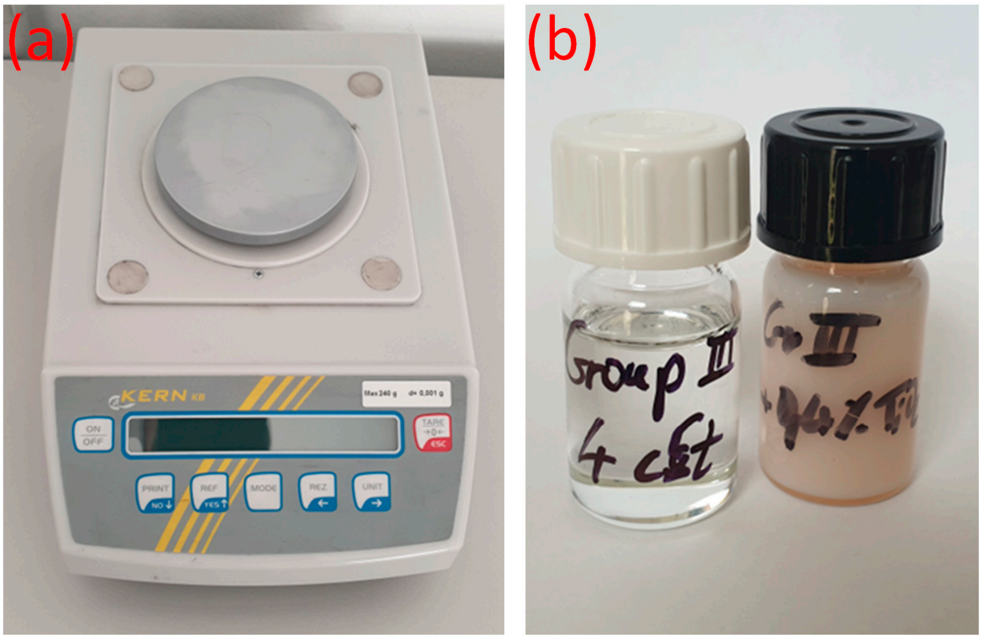

Figure 2. The used KERN magnetic stirrer (**a**); neat Group III 4 cSt and 0.4 wt% titania-added oil sample prepared for the tribological experiments (**b**).

This paper characterizes the tribological properties of the TiO_2 nanoparticles homogenized in Group III type base oil with the kinematic viscosity of 4 cSt (provided by MOL-LUB Ltd., Almásfüzitő, Hungary). For the tribological characterization measurements, an Optimol SRV®5 tribometer was used (Optimol Instruments GmbH, Munich, Germany), which is widely used for this kind of analysis [40]. The tribological effects of the prepared lubricant samples were analyzed between the contact surfaces of a ball and a disc specimen, where a sinusoidal oscillation movement of the ball was realized on the flat surface of the disc. The most important properties of both the ball and disc specimens correlate with the ISO 19291:2016 standard [41] and these specimens were provided by Optimol Instruments GmbH. (Munich, Germany). The ball is manufactured from a 100Cr6 material with a 10 mm diameter, 61 HRC hardness and 0.025 µm average surface roughness. The disc specimens were prepared from the same material (100Cr6); they have a 24 mm diameter and 7.9 mm height and they were spherodized and annealed with a surface hardness of 62 HRC. Their flat surfaces were lapped for an Ra value of between 0.035 and 0.05 µm and an Rz value of between 0.5 and 0.65 µm. Both specimens were thoroughly cleaned in an ultrasonic bath for 15 min under 50 °C temperature before being placed in the measurement chamber of the tribometer. The original peristaltic oil circuit of the SRV5 tribometer was used during these measurements to provide continuous lubricant flow into the contact surfaces of the specimens, which increased the lubrication efficiency and avoided the contact surface overheating via frictional heat [42]. The tribological measurement contained three main steps: a preconditioning phase where the starting conditions (100 °C temperature and 50 N load) are prepared; a low-load run-in phase (50 N for 30 s), where the required lubricant film can be formed under low load conditions; and a high-load long-term test (100 N for 2 h) to analyze the long-term tribological behavior of the lubricant sample. During the whole test, the main testing parameters (sinusoidal oscillation movement with 1 mm stroke and 50 Hz frequency, 100 °C specimen and oil temperature, 225 mL/h oil flow rate) remained constant. The prepared and homogenized lubricant sample was always kept in homogeneous status (continuous magnetic stirring) until it was filled into the oil circuit system of the tribometer. The mechanical setup of the tribometer can be observed in Figure 3. As the result of the tribological measurements, the controlling software of the Optimol SRV®5 tribometer calculated the integral average value of the measured coefficient of friction data to provide the necessary information about the frictional losses in each stroke of the oscillation movement. The formula for calculating the average integral value of the friction coefficient is presented in the following equation, where s is the stroke and μ is the friction coefficient.

$$FAI = \frac{1}{s_{max}} \cdot \int_{s_0}^{s_{max}} |\mu(s)| ds \quad (1)$$

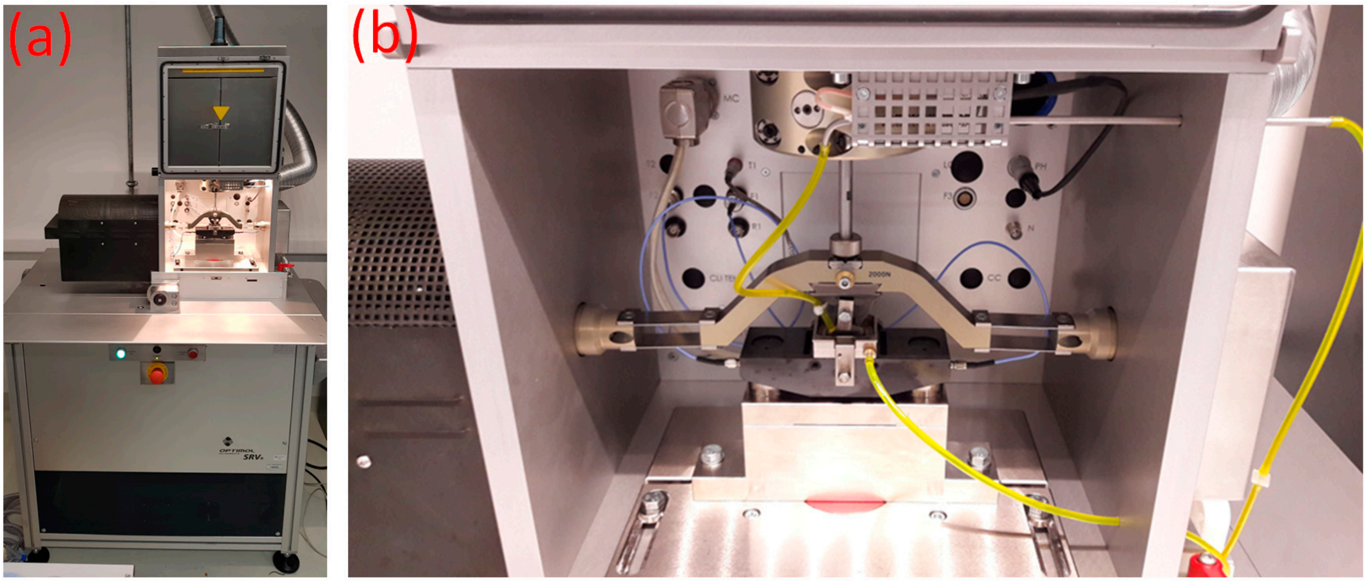

Figure 3. The used Optimol SRV®5 tribometer (**a**) and the mechanical setup of the executed tribological measurements including tubing for the continuous oil circuit (**b**).

Each lubricant sample was analyzed with at least 4 independent tribological measurements to ensure the accuracy of the calculation of average and deviation values of the friction coefficient data in the case of each nanoparticle concentration.

After a successful tribometer measurement, the worn surfaces were analyzed with several microscopes with the main goal of defining wear values and wear mechanisms. A Keyence VHX-1000 digital microscope (Keyence International, Mechlin, Belgium) with a maximal magnitude of 1000× was used to create images about the whole worn surfaces of the specimens and to measure the diameters of the circular worn surface on the disc specimen. The wear scar diameter values were measured parallel and perpendicular to the sliding direction separately and their average value was used as the MWSD (mean wear scar diameter) value [41]. A Leica DCM 3D confocal microscope (Leica Camera AG, Wetzlar, Germany) was also used during this research to digitalize the worn surfaces and their surroundings on the disc specimens. The wear volume was calculated according to the confocal microscope data, the original flat surface was calculated from the height data of untouched areas and the volume under this plane was considered as a missing material and its volume was calculated. The final step of the microscopical evaluation of the used specimens was the scanning electron microscope (SEM). A Hirox SEM-4000M type scanning electron microscope (Hirox Europe, Limonest, France) was used for this purpose, which also contains an energy-dispersive X-ray spectroscopy measuring sensor (Bruker Corporation, Billerica, MA, USA), which enabled the measurement of different elements of the outer layer of the surface.

4. Results

Figure 4 illustrates the evaluation of the measured friction coefficient integral average values of the investigated nanolubricant samples in the function of their titania concentration. A very clear tendency can be defined from this bar chart: TiO_2 nanoparticles homogenized into neat Group III base oil do not provide a positive effect for the lubricant in terms of friction reduction. Each prepared sample presented a friction coefficient increase between the values of 20 and 32%. However, it can also be observed that the measured error bars have reduced in each titania concentration, which indicates the positive stabilizing effect of the investigated nanoparticles.

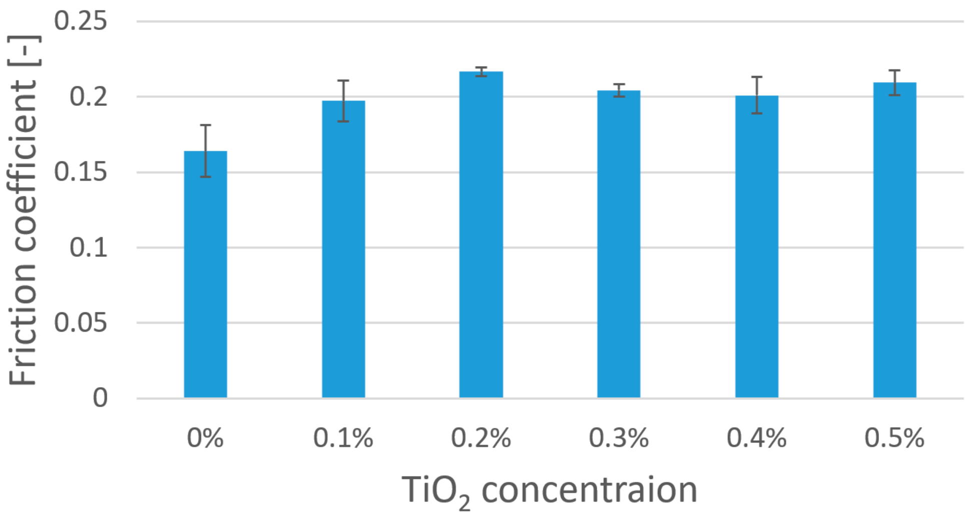

Figure 4. Comparison of the friction coefficient values of lubricant samples with various titania nanoparticle concentrations.

Figure 5 shows the comparison of the measured and calculated Mean Wear Scar Diameter (MWSD) values in the μm dimension. All the prepared nanolubricant samples decreased the measurable wear scar diameter values at each of the prepared TiO_2 concentrations. The measured tendency shows that the samples with higher titania concentrations (especially 0.4 and 0.5 wt%) work the best from the investigated samples; however, the 0.2 wt% sample also provides similar wear reduction properties as the 0.5 wt% sample. It is also clear that the error bars were also decreased, when compared with the reference results. The sample including 0.4 wt% titania nanoparticles showed the lowest MWSD results with a decreasing value of 32%.

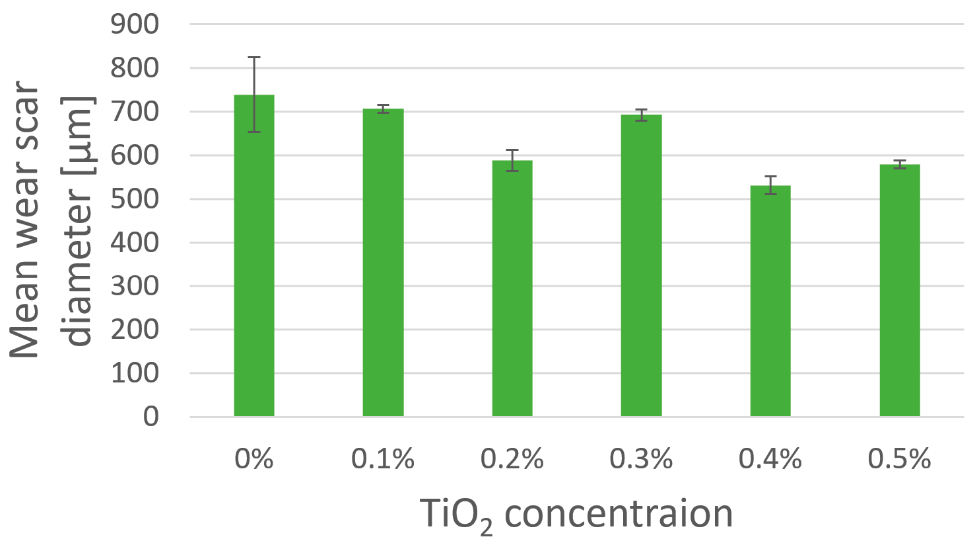

Figure 5. Comparison of the mean wear scar diameter values of lubricant samples with various titania nanoparticle concentrations.

The acquired digital microscope images of the worn disc surfaces with 0 and 0.4 wt% titania concentrations can be observed in Figure 6. The difference can clearly be defined: the addition of titania nanoparticles into the neat Group 3 base oil decreased the width of the wear scar. During a drastic wear process, the usually burned lubricant molecules (dark color on the surface) are removed by the connecting specimen and the worn surface becomes shinier. These shiny wear areas cannot be founded in the wear scars in the case of the titania-added samples, which leads to the deduction that the investigated TiO_2 nanoparticle eliminated the establishment of the drastic deep wear grooves since no metal-shining areas can be seen in the wear scar image acquired with 0.4 wt% titania containing nanolubricants.

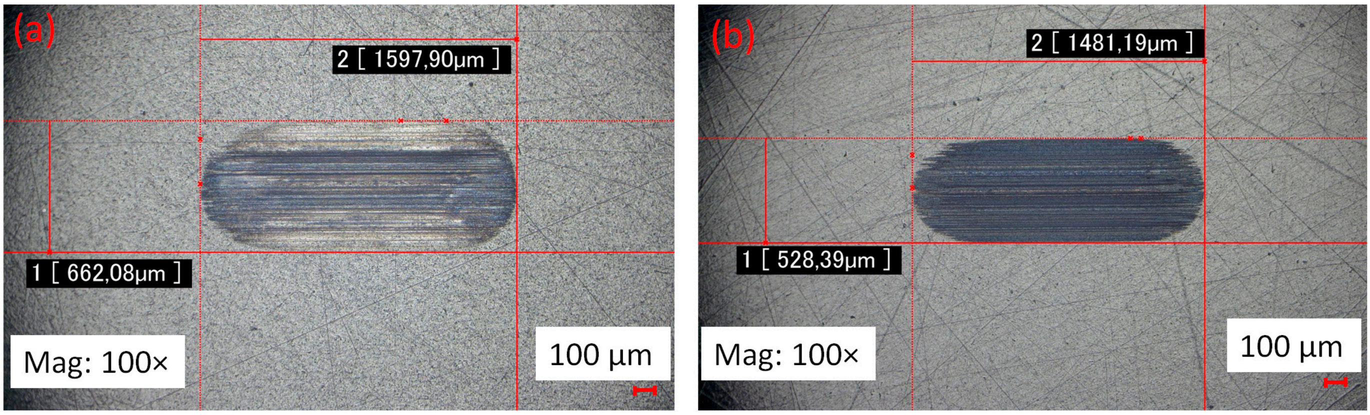

Figure 6. Acquired digital microscope images of the worn surfaces on the disc specimens with 0% (**a**) and 0.4% (**b**) titania NP concentrations.

Figure 7 presents the comparison of the nanolubricants according to the wear volume they generated during the tribological experiments. The bar chart clearly illustrates the differences between the lubricant samples with different titania concentrations and the positive antiwear effect of the titania nanoparticles. The tendencies according to wear volume and mean wear scar diameter are similar. The highest wear volume reduction was accomplished in the case of the 0.2 wt% titania-containing oil sample with a reduction of 57%, but the 0.5 wt% sample also shows identical wear-decreasing properties.

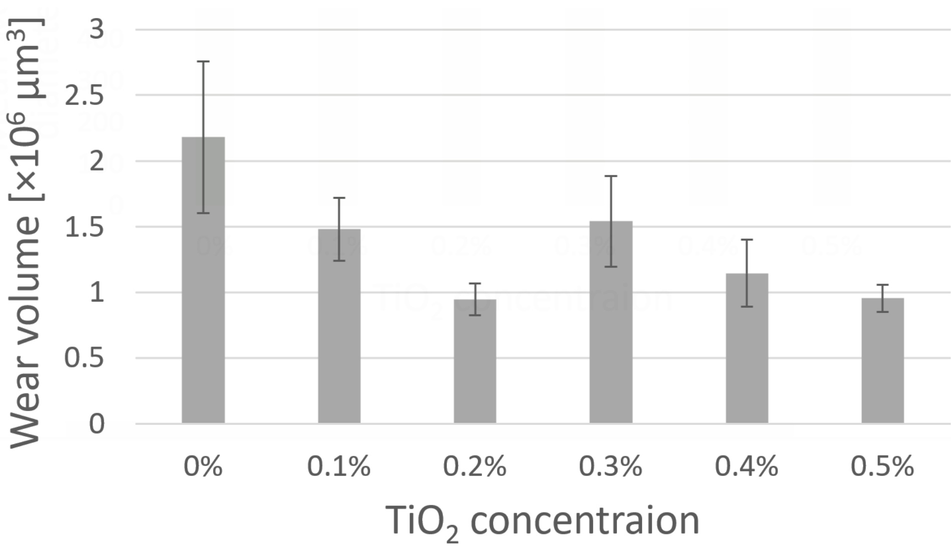

Figure 7. Comparison of the wear volume values of lubricant samples with various titania nanoparticle concentrations.

According to the acquired tribological results, the main influencing factors of the titania nanoparticles can be defined. The addition of TiO_2 nanoparticles into the neat Group III base oil increases the frictional losses significantly (friction coefficient increase of at least 20%). However, the wear reduction effect of the investigated oil samples is impressive: the measured MWSD values were reduced by 32% in the case of 0.4 wt% titania-containing lubricant and the calculated wear volume values were also dropped by 57% in the cases of the 0.2 and 0.5 wt% sample. Combining this information, the optimum concentration can be defined at 0.4 wt% because it provides the lowest possible friction coefficient and its wear reduction effect is excellent.

The viscosity of the Group III base oil with a titania content of 0.4% by weight was tested at a temperature of 100 °C. Table 1 shows the results obtained during the viscosity measurement in comparison with the reference. According to literature results, 0.4% titania nanopowder increases the viscosity of the base oil by more than 6 percent.

Table 1. Comparison of the viscosity measurement results of an oil sample containing 0.4 wt% titanium at 100 °C with Group III reference lubricating oil.

Parameter on 100 °C	Group III	Group III + 0.4% TiO_2	Change [%]
Dynamic viscosity [mPa·s]	3.432	3.663	+6.73%
Kinematic viscosity [mm^2/s]	4.373	4.653	+6.39%
Density [g/cm^3]	0.7848	0.7873	+0.32%

The scanning electron micrographs were taken with an accelerating voltage of 20 kV in secondary electron mode at a magnification of 1000. Figure 8 shows scanning electron micrographs and titanium intensity images of the wear tracks of a disc tested using an oil sample containing 0.4 wt% (optimum) nano-sized titania. The SEM images were taken on the center line of the wear track of the disc in the direction of movement. Figure 8a shows an image taken at the center of the disc, where the relative speed between the test bodies is the highest, and here, the formation of mixed friction is the most likely. Figure 8b shows an image taken in the middle of the dead center of the wear track of the disc. At this point, the relative speed is the lowest and reaches zero, so boundary layer friction is formed. Figure 8c,d show the intensity of the titanium element at the center of the wear mark (Figure 8c) and at the dead center of the wear mark (Figure 8d).

Based on the SEM images (Figure 8a,b), it can be established that the abrasion wear type is dominant on the entire wear track, the grooves of which are visible in the direction of movement. Traces of adhesive wear can be detected in both positions, however, it occurs in a higher proportion in the center of the wear track. EDX is a device suitable only for detecting elements. In the tribology system used during the tests, the titania nano-additive is the only component that contains titanium. Therefore, it can be concluded that all titanium signals entering the detector originate from the titania nano-additive. The figures showing titanium intensity indicate in red the areas from which titanium radiates with a greater intensity. Red areas contain more titanium than green, blue and black areas. Comparing Figure 8a,c, as well as Figure 8b,d, it can be concluded that small amounts of titanium occur uniformly in all areas of the wear track. It is mainly found in significant quantities in the deepest grooves of the wear marks. Based on the images, it can be established that the nano-sized titania additive fills the grooves of the wear track during its operation.

Figure 9 shows EDX spectra recorded at different points of the wear track of the disc. Figure 9a shows the EDX spectrum taken at the center of the wear track of the disc, while Figure 9b shows the spectrum taken at the dead center of the wear track of the disc.

The EDX spectra in Figure 9a,b show similar results; from this, it can be concluded that the elemental composition of the worn surfaces is similar and it is independent of the position. The iron tip is the highest because it provides most of the material of the disc. The primary alloying elements of the disc material are silicon and chromium. Carbon can also be found in the material of the disc, but it was mainly incorporated into the surface from the lubricating oil during the measurement. The origin of the oxygen peak can come from several sources: the disc's steel material; from surface oxidation; from the titania nano-additive. Since the origin of the oxygen is not clear, it is therefore not suitable for the detection of TiO_2. The signal of the titanium peak, marked in yellow in the spectrum, can only come from the presence of the titania additive, so it is used to determine the amount. Based on the intensity of the EDX signals, the titania content of the surface can be calculated; a summary is shown in Table 2.

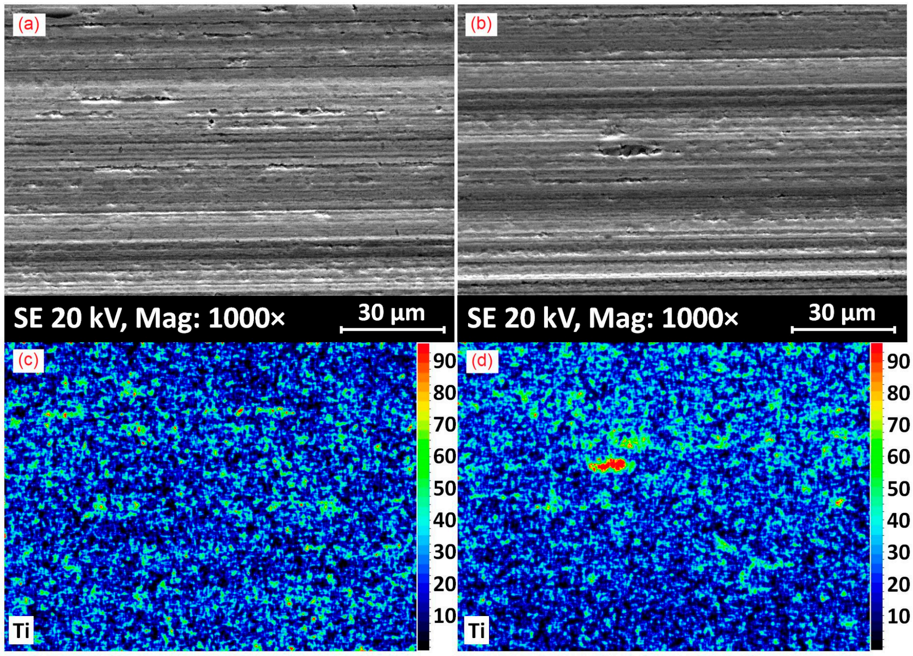

Figure 8. (**a**) SEM image was taken at the center of the wear track. (**b**) SEM image was taken at the dead center of the wear track. (**c**) Titanium intensity image in the center of the wear track belonging to (**a**). (**d**) Titanium intensity image in the dead center of the wear track belonging to (**b**).

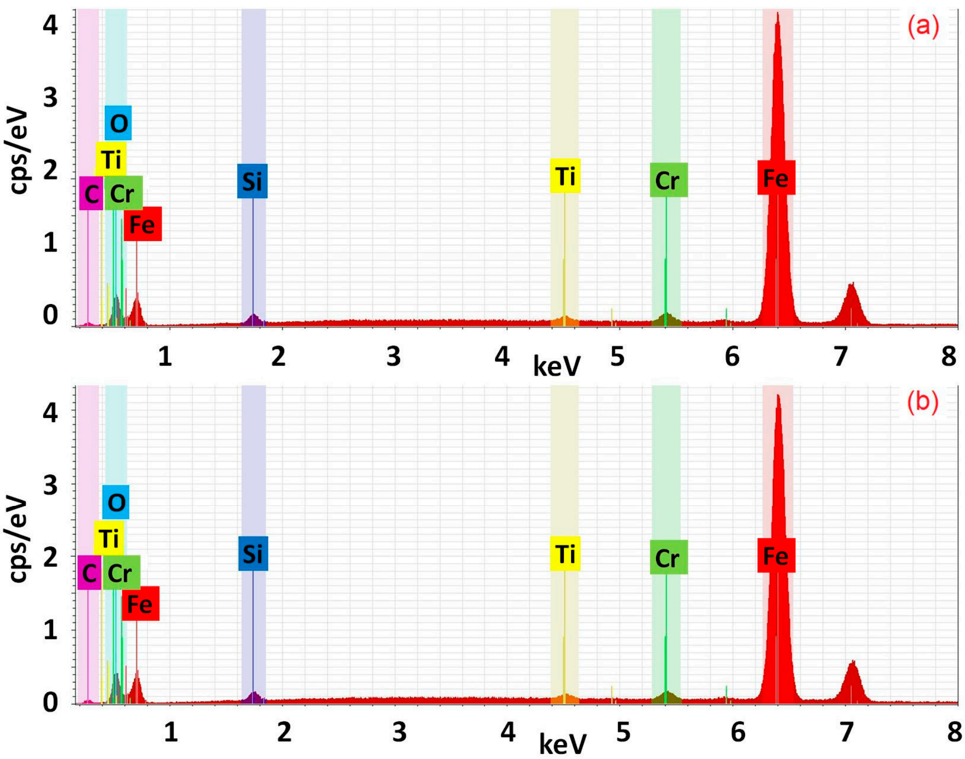

Figure 9. The upper figure (**a**) shows the EDX spectrum taken at the center of the disk (belongs to Figure 8a,c). The lower figure (**b**) shows the EDX spectrum taken at the dead center of the disk (belongs to Figure 8b,d).

Table 2. The table compares the elemental composition content [norm. wt%] of the unworn reference surface, at the center of the wear track and at the dead center of the wear track.

Element	Reference Surface	Center of the Wear Track	Dead Center of the Wear Track
Iron	88.73	91.72	73.21
Chromium	1.49	1.38	0.84
Silicon	0.75	1.39	1.04
Oxygen	2.33	3.7	2.25
Carbon	6.70	1.19	22.1
Titanium	0	0.62	0.56

From the results of the quantification, it can be concluded that a similar amount of titania nano-additives are found (settled in the valleys or embedded in the worn surface) in the entire area of the wear track. The unworn surface did not contain titania. The normalized titanium content of the center of the wear track was 0.62 wt%, while 0.56 wt% was found at the dead center. The high carbon content of the dead center shows that there was significant oil burning on the surface, which resulted from the higher friction of the dead center.

5. Discussion and Conclusions

This article demonstrated the wear analysis of titania nanoparticle-doped Group III base oil experimentally in a linear oscillating tribosystem. By using the titania nanoparticles, five Group III based lubricating oil samples were prepared (0.1; 0.2 . . . 0.5 wt% in concentration), which were suitable for tribology tests. The tribological tests of the lubricating oil samples were carried out by the Department of Propulsion Technology, Széchenyi István University, Győr. Lubricating oils were tested on a ball-on-disc oscillating tribometer by using continuous oil circulation. The friction was recorded during the measurements, then the worn surfaces were evaluated using a standard evaluation. The conclusions drawn can be compared with the literature.

- Based on the tribological results, the application of the titanium dioxide nanoparticles increases the friction by 20 to 32%. The consensus of the literature is that nano-sized titania particles have a friction-reducing effect, whereas the tests in this article report an increase in friction. While titania nanoparticles have been found to increase the viscosity of lubricating oil, titania was not able to prevent the massive friction-increasing effect of adhesion. In the future, it would be advisable to repeat the tests on the nanoparticles using some surface functionalization techniques on the nanoparticles.
- Titania nanoparticles could reduce the size of wear diameters by up to 32%. Titania protected the surface from forming deep grooves and reduced the wear volume parameters even up to 57%. These obtained results fully meet the expectations based on the literature.
- Titania increases the repeatability of the measurements, as the standard deviation of the measured values is significantly lower in every aspect. Publications have reported on the strengthening of the ability of nanoparticles to stabilize the tribological system.
- The optimum titania concentration in the used tribosystem can be defined at 0.4 wt%. The optimal concentration of the nano-additive in each tribological system used is different. The obtained result corresponds in magnitude with the optimum concentrations found in the literature.
- Scanning electron microscopy revealed that the primary wear type on the worn surface is abrasive wear. Abrasive wear is the main natural wear type characteristic of most tribological systems. Adhesive wear was found on the whole wear track, but it occurs more in the middle point of the wear track (highest relative speed area).
- Titanium intensity images revealed that all the worn area contains titania, but most of them can be found in the bottom of the deep wear grooves. EDX quantification

defined the amount of titanium content on the worn surface as 0.56 to 0.62%. A result consistent with the literature is that the titania-rich tribofilm increases wear resistance.

It can be stated that certain properties of Group III lubricating oil doped with titanium dioxide nanoparticles are not yet fully known and require further investigation. Although the nanoparticles showed a great anti-wear effect, they could not prevent the formation of adhesive wear. Surface modification of the nanoparticles is recommended for further investigation.

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