Experimental Analyses of the Additive Effect of TiO2 Nanoparticles on the Tribological Properties of Lubricating Oil

CORINA BIRLEANU
Technical University of Cluj-Napoca
MARIUS PUSTAN (Marius.Pustan@omt.utcluj.ro)
Technical University of Cluj-Napoca
MIRCEA CIOAZA
Technical University of Cluj-Napoca
ANDREEA MOLEA
Technical University of Cluj-Napoca
FLORIN POPA
Technical University of Cluj-Napoca
GLAD CONTIU
Technical University of Cluj-Napoca

Research Article

Keywords: Nanoparticles, Additive lubricants, Tribological properties, Rolling effect, Wear evaluation

Posted Date: December 17th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1123984/v1

Abstract

Titanium dioxide (TiO_2) is a promising lubricant additive for enhanced engine efficiency. In this study, pure base engine oil 10 W-30 was improved with titanium dioxide (TiO_2) nanoparticles at different concentrations and experimentally evaluated with the scope of tribological behavior improvement. The tribological tests were performed at ambient temperature as well as at 75°C using a four ball tribometer for 30 minutes. Due to their small particle size (approx. 21 nm), the TiO_2 nanoparticles were properly dispersed in oil based on optical microscopy evaluation. The tribological results indicate that the friction coefficient of engine oil with 0.075 wt.% TiO_2 reached 0.05 at 75°C, which was much lower that of pure oil (1.20), and at room temperature (23°C), it decreased from 1.8 for pure oil to 0.4 for oil with 0.075 wt.% TiO_2 due to the formation of a stable tribofilm formed by the MoS_2, MoO_3, FeS, and $FeSO_4$ composite within the wear track. The lowest wear volume was measured on samples tested at 75°C for the oil with 0.075 wt.% TiO_2. The TiO_2 additive lubricant effect on the tribofilm properties led to a decrease in friction and wear at an operating temperature of 75°C. The main objective of the paper is to present the recent progress and, consequently, to develop a comprehensive understanding of the tribological behavior of engine oil mixed with TiO_2 nanoparticles.

Highlights

Various advanced strategies for improving the tribomechanical performance of nanolubricants based on metal oxide particles, especially TiO2, are reviewed.

The plausible tribo-mechanism of enhanced lubricating oil properties by adding TiO2 nanoparticles from each strategy is discussed.

The conclusive outlook, challenge, and suggestions for future development of engine lubricants based on TiO_2 which play a decisive role in the improvement of the tribological performance. Additionally, spherical TiO_2 has a probable ball-bearing lubrication effect during the friction process.

1. Introduction

Research conducted in recent years on the addition of nanoparticles (NPs) to oils used in industry by increasing the load-bearing capacity of friction parts in mechanical systems has been friction modifiers and anti-wear additives. Moreover, increasing the severity of loading and speed conditions in machines is a constant challenge for tribologists to develop improved solutions to increase the performance properties of used oil. Nanoparticles, due to their small size, are able to access areas with extremely small surface roughness and therefore have great potential in improving the tribological properties of lubricants and contact surfaces. Numerous studies have been conducted in the last two decades regarding the use of nanoparticles as lubricating additives [1–3]. The addition of nanoparticles to the base oil can reduce friction and wear, and it can be said that the nanoparticles could be beneficial lubricating additives, although some may be hard and abrasive [4, 5–7]. In recent years, various nanoparticles have been investigated [4, 6–8]. The nanoparticles used are generally metals such as Cu, Ni, Mo, Ag, and Pd; metal oxides including TiO_2, SiO_2, ZnO, ZrO_2, and CuO; and sulfides WS_2, MoS_2, and PbS [2].

Several hypotheses emerge from the open literature about how nanoparticles contribute to the reduction of friction and wear under different laboratory testing conditions. However, useful information can be detached if prototypical materials are used together with a balance between the applied mechanical parameters (loads, speeds, temperatures, contact pressures) and surface conditions.

The transfer and adhesion of the nanoparticles leads to the change of the surface condition, the self-reduction, and the formation of a thin TiO_2 tribo-film which conduct to the decrease of the coefficient of friction, of the pressure and the temperature in the contact area, therefore of the wear phenomenon.

The addition of TiO_2 nanoparticles to the lubricating oil showed stable friction due to the formation of protective films on the worn surfaces [9]. Shenoy et al. [10] analysed the influence of TiO_2 nanoparticles in lubricating oil. The results obtained showed a higher bearing capacity by approximately 35% compared to the use of lubricating oil without the addition of nanoparticles. The experiments performed by Kao and Lin [11] using an alternative sliding tester to analyse friction and wear in the presence of additive rapeseed oil showed that there was an 80.84% reduction in mean surface roughness. The average diameter of TiO_2 was 50 nm, and the particle concentration was 5 weight percent (wt.%). Using a low concentration of TiO_2 nanoparticles is enough to improve the tribological characteristics. The coefficient of friction and the wear scars decreased by approximately 15.2% and 11%, respectively [12].

Several studies have been conducted on nanoparticles as oil additives [10–13]. The particle size of TiO_2 affected the wear behavior of the composite material [14]. It was found that the microscale particles of TiO_2 damaged the surface due to severe adhesion and abrasion. The surface damage due to nanoscale TiO_2 particles was due to slight abrasion. More investigations have been carried out on TiO_2 as a coating material [12–15] or reinforcement in composites [10] for better tribological performance [13].

The lubrication mechanism in the presence of nanoparticles produces (Figure 1): (a) the surface properties will be modified and two friction surfaces will be separated with tribo-film formation, thus offering promising tribological performance; (b) the nanoparticles roll between the friction surfaces, reducing friction and wear; and (c) the heat and pressure generated during operation lead to the compaction of the nanoparticles following wear, which is considered a mending effect of the surface and a polishing effect [7].

In this paper, the antifriction and antiwear behaviors of TiO_2 nanoparticle suspensions in 10 W-30 oil with different percentages (0.010, 0.025, 0.050 and 0.075 wt.%/v) were evaluated using a tribometer with four balls. The results present the influence of the nanoparticle percentage on the tribological behaviour of the mixed oil, the evaluation of worm surface structure through the various operating conditions tested by scanning electron microscopy (SEM), and the depth of wear marks on the spheres measured using the Alicona Inginite Focus G5 Microscope.

A 4-ball tribometer was used in this study, for which the friction force (the coefficient of friction) between the samples was continuously recorded according to the normal load and the elapsed time. Four nanooil samples were prepared and tested repeatedly with various specimens from the 4-ball tribometer to evaluate the direct effect and the surface-enhancing effect of nanoparticles in the lubricating oil.

Therefore, the purpose of this paper is dedicated to finding the possibility of tribological performance improvement of conventional engine oil using TiO_2 nanoparticle additives. This promising technology has a large impact on fuel consumption and engine durability for a greener future.

2. Samples Description

Experimental studies involve the formulation of stable TiO_2-based nanolubricant samples at different concentrations. The physicochemical properties, such as density, viscosity and viscosity index, were measured using an automated SVM 3000 Anton-Paar rotational Stabinger viscometer. Density was measured using a vibrating U-tube densimeter, and for the determination of viscosity, a Peltier element was used to thermoregulate the samples.

2.1 Materials

Against the background that TiO_2 is best suited for many tribological applications (including solid lubricants) due to its excellent tribological behavior, these nanoparticles were chosen for the current investigation. Commercial TiO_2 Degussa P25 nanoparticles supplied from Sigma–Aldrich and Motul 5100 4T 10 W-30 engine oil were used in the formulation of nanolubricant samples. The average sizes of the TiO_2 nanoparticles were 18–21 nm.

Table 1
Properties of commercial TiO_2 Degussa P25 and Motul 5100 4T 10 W-30 engine oil

Raw materials	Properties	Value
TiO_2 Degussa P25	Crystalline phases	75% anatase, 25% rutile
	Average particle size	21 nm
	Surface area	>30 m2/g
	Density	3900 kg/m3
Motul 5100 4T	SAE Viscosity grade	10 W-30
	Density at 20°C	871 kg/m3
	Viscosity at 40°C	74.6 mm2/s
	Viscosity at 100°C	11.5 mm2/s
	Pour point	-36°C
	Flash point	226°C
	Total basicity number (TBN)	7.5 mg KOH/g

Table 2
Concentrations of the prepared nanolubricants

Lubricant sample	LS	L0	L1	L2	L3
TiO_2 (wt.%)	0	0.010	0.025	0.050	0.075
Pure base oil (%)	100	99.99	99.75	99.50	99.25

The properties of the raw materials are presented in Table 1. The varying concentrations of TiO_2 for the engine oil used in the experiments were 0.010, 0.025, 0.050 and 0.075 wt.%, as shown in Table 2. To demonstrate the effect of nanoparticles on the engine oil additives, tribological tests were conducted using commercial lubricant engine oil - Motul 5100 4T10 W-30.

2.2 Nanolubricants preparation

The mixing of nanoparticles with engine oil is an important step towards the improvement of engine oil quality. Different amounts of TiO_2 nanoparticles (Table 2) were dispersed into engine oil, and 0.2 mM Triton X surfactant was added to increase the stability of the nanolubricants. The 0.2 mM Triton X surfactant plays an important role in blending the nanoparticles in a manner that makes them soluble in the engine oil, also providing stability for the nanoparticles, preventing the agglomeration of the nanoparticles within engine oils. Moreover, to increase the stability over time, the prepared suspensions were subjected to magnetic stirring, followed by ultrasound treatment for 30 minutes.

The physicochemical properties of engine oil and TiO_2 nanolubricants are presented in Table 3. It can be observed that with an increase in the TiO_2 amount in the engine oil, the density tends to increase by 0.2% (from 862 kg/m3 for the base oil up to 864 kg/m3 for the nanolubricant, which contains 0.075 wt.%/v) due to the high density of the nanoparticles (3900 kg/m3), even if the concentration of TiO_2 is very small. Additionally, cinematic viscosity at both 40°C and 100°C tends to increase with TiO_2 concentration in nanolubricants to 3% and 4%, respectively (from 89.7 mm2/s to 92.3 mm2/s and from 13.6 mm^2/s to 14.2 mm^2/s, respectively). According to Ali et al. [16], this behavior is related to the fact that the nanoparticles act as catalysts in a cracking reaction and heat transfer properties. The high viscosity of the nanolubricant oils improves the lubricating property because it reduces friction and prevents rapid wear. The viscosity index increases up to 158 when TiO_2 nanoparticles are added into the oil, which means that the variation of viscosity with temperature is lower for nanolubricant oils than base oil.

Table 3
The physicochemical properties of engine oil and TiO_2 nanolubricants

Sample	**Density at 15°C [kg/m^3]**	**Cinematic viscosity at 40°C [mm^2/s]**	**Cinematic viscosity at 100°C [mm^2/s]**	**Viscosity index**
LS (pure base oil)	862	89.7	13.6	154
L0	863	91.6	14.1	158
L1	863	92.1	14.1	158
L2	863	92.0	14.1	158
L3	864	92.3	14.2	158

2.3 Ball materials

The standard ball test material was 52100 grade 25 chrome alloy steel, 12.7 mm in diameter with a surface roughness (R_a) of 0.1 µm, extra polish (EP) grade of 25 and hardness of 54 to 58 HRC. Four new balls were used for each test. Before starting a new test each time, the balls were cleaned with a technical cleaner (isoparaffinic-based solvent cleaner) and wiped dry using tissues. The chemical composition and mechanical properties of the ball material are listed in Table 4.

Table 4
Chemical and mechanical properties of ball material

Chemical properties						
%Fe	%C	%Si	%Cr	%P	%S	%Mn
96.5 – 97.3	0.93 – 1.1	0.15 – 0.35	0.14 – 0.16	0 – 0.025	0 – 0.015	0.25 – 0.45
Mechanical properties						
Hardness (HRC)	Tensile strength (MPa)	Yield strength (MPa)	Young's modulus (GPa)	Poisson’s ratio (-)	Roughness R_a (μm)	
54 - 58	2100 - 2200	2000	200	0.3	0.1	

3. Experimental Method And Device

The American Society of Lubrication Engineers has published a catalog of friction and wear testing devices that describes in detail over 230 different tribometers [7]. Each device has its strengths and weaknesses. For this work, we used the four-ball wear test geometry, which has been selected to provide the following test conditions: high contact pressures that ensure operation in boundary lubrication mode; good control of the operating parameters of load, temperature, speed, operating time, atmosphere; high sensitivity of wear and friction measurements; simple samples for testing, small dimensions and easy manufacture.

The four-ball tester is an excellent tool for checking and determining the quality of lubricants and additives. This tribometer can be used to determine the wear preventive properties (WPs), extreme pressure properties (EPs) and friction behaviour of lubricants. The widespread acceptance of Four Ball Tester test results makes it an excellent tribological device.

This tribometer consists of a device where an upper ball can be rotated and is in contact with three fixed balls that are immersed in the oil sample. Different loads are applied to the ball by weights applied to a system with the load lever. The upper rotary ball is held in a special chuck located at the lower end of the vertical axis of an electric motor and rotates at a constant speed. The lower fixed balls are held in contact with each other in a steel pot by a clamping ring and a locking nut. The arrangement is illustrated in Figure 2. The basic sample configuration (Fig. 3) consists of a tetrahedral arrangement of four balls.

These tests were carried out under the American Society for Testing and Materials (ASTM) condition and ASTM D 4172 method test B. The tests were conducted under dry conditions at a room temperature RT $(23 \pm 2)^{o}C$ and then at $(75 \pm 2)^{o}C$ and relative humidity RH (35 ± 2)%, the speed (1200 ± 60) rpm, the time test (30 ± 1) minutes and the load: (396 ± 4) N. The tests were repeated at least three times for every measurement. All presented results in this work are the arithmetic mean value of the measured values, unless otherwise stated. The corresponding standard deviation is indicated by the error bars, describing the scatter of the results.

Experimental procedure involves the following steps:

a. Before starting to do the experiment, all parts of the balls were cleaned with acetone and then wiped;
b. A four-ball machine was set up with the correct speed, temperature and time;
c. Three clean balls were inserted into the ball pot, and then the ball lock ring was placed inside the ball pot and around the three balls;
d. A lock nut was tied on the ball pot, and torque wrench was used to fasten it with a force of 68 Nm.
e. One clean ball in collet was put in and inserted into the tapper at the end of the motor spindle;
f. Approximately 10 ml of test lubricant was added to the ball pot assembly, and the lubricant had to become 3 mm above the tip of the ball.
g. A ball pot assembly was placed on the antifriction disk inside the machine and under the spindle.
h. Thermocouple wire was connected to ball pot assembly;
i. Load was added or removed to the loading arm until digital monitoring showed the correct load for the experiment;
j. In ASTM D 4172 method test B, the amount of load is 396 N, and in the four balls test machine, the load cell is fitted at a distance of 80 mm from the center of the spindle;
k. The last step was to measure the wear scars on the three lower balls with the help of an image acquisition system. The wear was measured with the average of horizontal and vertical scars with SEM, and the depth of wear marks on the spheres was measured using an Alicona Inginite Focus G5 microscope.

The viscosity is a very important parameter for a lubricant, as it affects the film thickness and the wear rate of the sliding surface. It is used for the identification of individual grades of oil and for monitoring the changes occurring in the oil while in service. Increasing the viscosity normally shows that the used oil has been deteriorated by contamination or oxidation. Additionally, decreased viscosity usually indicates dilution of the oil. The oil viscosity was measured with a viscosity meter at experimental temperatures of 23°C and 75°C. In test B method ASTM D 4172, the load was 396 N, and in the four-ball test machine, the load cell was mounted 80 mm from the center of the shaft. In addition, the wear was measured with the average of horizontal and vertical scars with SEM, and the depth of wear marks on the spheres was measured using an Alicona Inginite Focus G5 microscope. The duration of the test was selected to ensure that the running-in period was less than 30% of the total duration of the test.

4. Results And Discussion

4.1 Wear Scar Images of Balls

Micrographs of the wear scar formed on the balls for each of the formulations are shown in Figures 4 and 5. The addition of TiO_2 led to reductions in the diameter of the wear scar.

Figures 4 and 5 reveal the wear scar maps of the tested ball sliding against the bearing steel balls. This shows that the wear degree of the samples containing TiO_2 was obviously improved compared to that of the base oil. When the base oil was a lubricant, the worn surface of the ball presented black sediment, which confirmed that the main component was Fe resulting from ball-on ball milling. Moreover, the 0.01 wt.% and 0.025 wt.% samples also presented back sediment, but the wear radii were visibly reduced. In particular, the radius of the 0.075 wt.% oil sample in the stabilized state after rubbing was smaller than that of the other samples, showing the superior anti-wear performance of this sample.

To further investigate the wear mechanism, SEM images of worn surfaces of the lower balls lubricated by the base engine oil and the engine oil samples containing 0.01, 0.025, 0.050 and 0.075 wt.% TiO_2 nanoparticles were investigated. The tests were performed at two different working temperatures, 23°C (RT) and with oil heated to 75°C.

Following the evaluation of the wear traces with SEM, radius differences of the circular wear trace are observed, and the radius difference is approximately 5-10%. This should not greatly influence the mechanism of wear (generation of wear residues, increase of the tribo-layer, etc.).

Figure 4 shows that for samples LS and L0, there was obvious plowing and some pits on the worn track, which were due to the second local rupture of debris during the sliding process; moreover, the friction of debris at the sliding interface clearly furrows on the worn surface.

Figure 4 (L2 and L3) shows that the worn surface presented finer mesh-like grooves, in agreement with the COF result in Figure 11. For the 0.05 wt.% sample, the worn surface was covered by fine grooves and detachments after the rolling test, as shown in Figure 4 (L1), and the mechanism of wear was dominated by microplowing. Furthermore, Figure 4 (L2 and L3) shows that the wear scratch was almost invisible; through a local zoom of the images in Figure 4, slight furrows of wear could be observed. This is mostly attributed to the increase in $TiO_{2,}$ which could reduce the wear of frictional interfaces. This indicates that TiO_2 played a lubricating role and prevented wear in the rolling process. The above results are in agreement with the tribological results showing the decrease in the friction coefficient in Figure 11.

The wear scar diameter of each of the three bottom test balls was measured to determine the lubricity performance of the test lubricant. In general, the larger the wear scar diameter is, the more severe the wear, but we also consider the depth of the wear trace. The wear scar diameter was determined for each of the three fixed balls.

The temperature of the test lubricants was measured by a thermocouple attached to the four-ball tester to record the temperature changes throughout the duration of the experiment.

The base oil and nano-oils were tested at temperatures of 23°C and 75°C (close to the temperature service for engine oil). Increasing the temperature results in nanoparticle movement, which is associated with reducing the fluid resistance over the flow; therefore, the viscosity is reduced. With respect to viscosity, it is clear that either of the base oils or nano-oils are non-Newtonian fluids. However, the temperature of the contact point for the balls is also influenced by the sliding speed. A sliding speed of 0.80 ms^{-1} (calculated based on input parameters) was selected to provide the minimum and extreme heating due to sliding.

4.2 Wear Depth Scar on the Balls

The depth of the wear scar on the spheres was measured using an Alicona Inginite Focus G5 microscope. The surfaces were scanned with a microscope using 50x magnification, and the light source was coaxial with the eyepiece (lenses) and supplemented with a light ring. Scanning was performed using Image Field mode with a vertical resolution between 0.003 and 0.032 microns and a horizontal resolution of 2.13 microns. The duration of a scan was between 1.5 and 3 minutes. The average scan height was 0.150 mm. This gives a Vertical Dynamic of 150/0.032=4687.5.

The evaluation of the wear depth was performed by measuring the distance from the ideal circle, constructed using a fixed 6.35 mm beam with the Measure Circle function. The traces of the intersection between the scanned surface and the plane in which the depth measurement was performed were used to orient and position the ideal circle. The depth of wear (difference between the ideal circle and the trace on the sphere) was measured using the measure height step function or maximum distance. The 2D profiles of the worm surfaces for different lubricant oils after the wear test are shown in Figs. 6 and 7.

Compared with pure oil, TiO_2 had a significant improvement in the wear surface. After the wear test at RT, only small groves could be observed, and the wear mechanism was mainly formed by microplowing. Although the wear depth of the 0.01 wt.% sample was much smoother than that of the base oil, microplowing still existed, with a corresponding wear depth of 1.2 μm – RT and 0.41 μm – 75°C. Moreover, the anti-wear property is improved with the amount of TiO_2. This indicates that TiO_2 in engine oil prevents the plowing wear that existed in the control sample.

Figure 8 shows a chart of the amount of ball wear, as measured using the Alicona Inginite Focus G5 microscope. Very little protection was provided by the base oil, but the addition of nanoparticles to the base oil significantly reduced wear.

The wear rate of the lower balls at RT was somewhere 70 x $^{103\ \mu m3}$ for the base oil, gradually reaching up to 10 x $^{103\ \mu m3}$ for the concentration of 0.075 wt.% TiO_2. At a temperature of 75°C, the wear decreased to 33 x $^{103\ \mu m3}$ for the base oil, and then with the addition of wt% TiO_2 nanoparticles, it decreased to 5 x $^{103\ \mu m3}$. The measurements of the wear depths produced on the balls were accurate and repeatable with the help of the Alicona Inginite Focus G5 microscope.

In the current study, the authors tried to avoid overloading the tribocouple due to a high risk of layer deformation and change in the wear mechanism. Considering the wear rates of the balls studied by the authors (33 – 70 x $^{103\ \mu m3}$) at RT, it can be concluded that the wear of the balls is a few orders of magnitude larger for balls lubricated at 75°C. This can be explained by the fact that the connecting rods are always in contact, and therefore, the phenomenon of continuous overheating occurs.

No transfer film was observed on the balls at a slip velocity of 0.80 ms^{-1}. However, the tests were accompanied by vibrations and unwanted noise.

4.3 Friction property of lubricating oils with TiO_2 additives

The tribological performance of engine oil (Motul 5100 4T10 W-30) with TiO_2 additive loading as a lubricant additive is shown in Figure 10. The coefficient of friction (COF) of engine oil with different additive TiO_2 amounts was measured at an applied load of 10 N at the arm of the tribometer, 396 ±4 N normal load applied on balls and rotation 1200 rpm, as presented in Figures 2-3. Relative fluctuations in the friction response of base engine oil were observed in comparison to the additive response, and the COF was found to increase with time in the initial stage during the running period.

The coefficients of friction were remarkably reduced by the addition of TiO_2 nanoparticles to the base lubricant. At a normal applied force of 396 N, the coefficient of friction of the nanolubricant was reduced by approximately 60% of the COF value for the base lubricant at RT and by approximately 80% at a temperature of 75°C.

Clearly, the nanolubricant with more TiO_2 nanoparticles had the best coefficient of friction (Figure 9). These results indicate that the TiO_2 nanoparticles decrease the ball-to-ball friction contact compared to the base lubricant.

The medium lowest COF of 0.01 was obtained by the oil sample with 0.075 wt.% TiO_2 under a 75°C lubricant temperature. Moreover, Figure 10 shows the influence of particle concentration on the COF of oil suspensions, indicating that the average COF was influenced by the TiO_2 concentration. The average COF obviously fell from 0.112 to 0.05 in the range of 0.01 wt.% to 0.075 wt.% TiO_2, reflecting that the addition of nanoparticle lubricants straightened the sliding response when stabilizing additive amounts below 0.025 wt.% TiO_2. However, the average COF showed a slightly decreasing trend from 0.010 – 0.088 in the range of 0.010 wt.% to 0.025 wt.% at RT. On the other hand, at 75°C, the average COF obviously fell from 0.095 to 0.015 in the range of 0.01 wt.% to 0.075 wt.% TiO_2. Furthermore, the COF tended to be stable after rubbing, and the corresponding average COF in the stable period for higher concentrations of TiO_2 presented a lower antifrictional property, as shown in Figures 9 and 10. The relevant tribological mechanism at RT is due to TiO_2 particles at higher concentrations accumulating in the inlet of the ball-on-ball contact area, which causes an insufficient supply of lubricant and starvation in the contact area.

The running-in period is of great significance to the regulation of tribological performance to a certain extent. Reducing the running-in period is beneficial to improving the antifrictional property. The formation of a boundary lubrication film is the main reason for the stability of the friction coefficient. The coefficients of friction stabilized in the second part of the test time. The rubbing period of nano-oil with a 0.1 wt.% concentration lasted longer than that of the others with a time of 780 s. In addition, it is noteworthy that the rubbing time obviously decreased with increasing concentration. The 0.05 and 0.075 wt.% samples had the shortest rubbing time in terms of friction properties.

The friction coefficient was calculated according to IP-239 and is expressed as follows:

$$\mu = 0.22248 \cdot \frac{1000 \cdot \mathrm{T}}{\mathrm{F}} \qquad (1)$$

where T is the frictional torque in kgmm and F is the applied load in kg [12]. The frictional torque data were recorded by software, and the friction coefficient was calculated.

4.4 Flash Temperature Parameter

The flash temperature parameter is a unique number that gives us indications of the critical flash temperature above which the lubricant used will be out of use [16]

For working conditions in the four-ball tribometer, the flash temperature parameter is:

$$\mathrm{FTP} = \frac{\mathrm{F}}{\mathrm{d}^{1.4}} \qquad (2)$$

A flash temperature parameter (FTP) was calculated for all of the experimental conditions according to Eq. 2. In this equation, F is the normal load in kilograms and d is the mean wear scar diameter in millimeters at the particular load. A detailed explanation of the parameter is given by Lane [16, 17].

High values for the flash temperature parameter indicate that the lubricant shows good performance with a reduced possibility of lubricant breakdown [15].

Figure 11 shows the plot of TiO_2 percentage vs. flash temperature parameter (FTP) for different testing temperatures, more exactly room temperature RT and 75°C. From the figure, it can be seen that the maximum and minimum FTPs were obtained from 0.075 wt.% contaminated lubricant and pure lubricant, respectively. The maximum FTP value means that good lubricating performance occurred, indicating a lower possibility of lubricant film breakdown. This phenomenon has also been observed by other researchers [11]. This seems to indicate that TiO_2 nanoadditives are a potential anti-wear additive for lubricating oil. The 0.075 wt.% TiO_2 in this investigation improved the lubricant performance based on the higher value of FTP observed compared with pure lubricant. The graphs also show the effect of temperature on the FTP of lubricants.

5. Conclusions

For the tests performed on a four-ball wear machine with different percentages of TiO2-contaminated lubricant, the conclusions drawn are as follows.

The wear of the ball specimens decreases with the increase in wt.% TiO_2 addition. Compared with pure lubricant, 0.075% TiO_2 improves the lubricant performance based on the higher value of the flash temperature parameter (FTP).

The medium lowest COF of 0.01 was obtained by the oil sample with 0.075 wt.% TiO_2 under a 75°C lubricant temperature. The average COF obviously fell from 0.112 to 0.05 in the range of 0.01 wt.% to 0.075 wt.% TiO_2, reflecting that the addition of nanoparticle lubricants straightened the sliding response when stabilizing additive amounts below 0.025 wt.% TiO_2. On the other hand, at 75°C, the average COF obviously fell from 0.095 to 0.015 in the range of 0.01 wt.% to 0.075 wt.% TiO_2. The lowest COF was obtained for the 0.075 wt.% TiO_2 oil sample, which dropped by approximately 60% compared to the pure base oil at RT and by approximately 80% at a temperature of 75°C. Furthermore, the rubbing time obviously decreased with the increase in TiO_2.

The main wear type of the worn surfaces lubricated by the engine base oil with TiO_2 could be attributed to slight ploughing wear. Pure oil presented an obvious furrow and indentation, with a corresponding maximum depth of 1.2 μm. From physical observations on worn surfaces of specimens, it can be suggested that nano-oil with TiO_2 (0.075 wt.%) acts as an anti-wear lubricant additive. Micrographs showed that wear scar surfaces in the 0.075% TiO_2-contaminated lubricant tests appear to be much smoother, thus having less material transfer.

TiO_2 plays a decisive role in the improvement of the tribological performance. Additionally, spherical TiO_2 has a probable ball-bearing lubrication effect during the friction process.

Declarations

Author contributions

C.B. and M.P. conceived the experiments, M.C., A.M., F.P. and G.C. conducted the experiments, C.B., M. C and G. C analysed the results, C.B. and M.P. supervised the work. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Correspondence and requests for materials should be addressed to M.P.

References

1. W. Dai, B. Kheireddin, H. Gao, H. Liang, Roles of nanoparticles in oil lubrication. Tribol. Int. 102, 88–98 (2016). https://doi.org/10.1016/j.triboint.2016.05.020
2. K.G. Binu, B.S. Shenoy, D.S. Rao, R. Pai, Static characteristics of a fluid film bearing with TiO_2 based nanolubricant using the modified Krieger–Dougherty viscosity model and couple stress model, Trib. Int. 75, 69–79 (2014) https://doi.org/10.1016/j.triboint.2014.03.013
3. S. Ingole, A. Charanpahari, A. Kakade, S.S. Umare, D.V. Bhatt, J. Menghani, Tribological behavior of nano TiO_2 as anadditive in base oil. Wear 301, 776–85 (2013). https://doi.org/10.1016/j.wear.2013.01.037
4. N.G. Demas, R.A. Erck, C. Lorenzo-Martin, O.O. Ajayi, G.R. Fenske, Experimental evaluation of oxide nanoparticles as friction and wear improvement additives in motor oil. Journal of Nanomaterials, 2017. https://doi.org/10.1155/2017/8425782
5. Y.Y.Wu, W.C.Tsui, T.C.Liu Experimental analysis of tribological properties of lubricating oils with nanoparticle additives, Wear, 262, 819–825 (2007). https://doi.org/10.1016/j.wear.2006.08.021
6. K. Lee, Y. Hwang, S. Cheong, Y. Choi, L. Kwon, J. Lee, S.H. Kim, Understanding the Role of Nanoparticles in Nano-oil Lubrication. Tribol Lett 35, 127–131 (2009). https://doi.org/10.1007/s11249-009-9441-7
7. Y.J.J. Jason, H.G. How, Y.H. Teoh, H.G. Chuah, A Study on the Tribological Performance of Nanolubricants. *Processes, 8*, 1372 (2020). https://doi.org/10.3390/pr8111372
8. F.; Ilie, C. Covaliu, Tribological Properties of the Lubricant Containing Titanium Dioxide Nanoparticles as an Additive. Lubricants 4, 12 (2016). https://doi.org/10.3390/lubricants4020012
9. B. Shenoy, K. Binu, R. Pai, D. Rao, R.S. Pai, Effect of nanoparticles additives on the performance of an externally adjustable fluid film bearing. Tribol. Int. 45:38–42 (2012). https://doi.org/10.1016/j.triboint.2011.10.004
10. M.J. Kao, C.R. Lin, Evaluating the role of spherical titanium oxide nanoparticles in reducing friction between two pieces of cast iron. J Alloys Compd 483: 456–9 (2009). https://doi.org/10.1016/j.jallcom.2008.07.223
11. S. Arumugam, G. Sriram, Preliminary study of nano and micro scale TiO_2 additives on tribological behavior of chemically modified rapeseed oil. Tribol Trans 56:797–805 (2013). https://doi.org/10.1080/10402004.2013.792977
12. Y. Wang, T. Lei, L. Guo, B. Jiang, Fretting wear behaviour of microarcoxidation coatings formed on titanium alloy against steel in unlubrication and oil lubrication, Applied Surface Science 252(23) 8113–8120 (2006). https://doi.org/10.1016/j.apsusc.2005.10.032
13. S. Ingolea, A. Charanpahari, A. Kakade, S.S. Umare, D.V. Bhatt, J. Menghani, Tribological behavior of nano TiO_2 as an additive in base oil, Wear, 301, 776–785, (2013). https://doi.org/10.1016/j.wear.2013.01.037.
14. M.I.H.C. Abdullah, M.F.B. Abdollah, H. Amiruddin, N. Tamaldin, N.R.M. Nuri, The potential of hBN nanoparticles as friction modifier and antiwear additive in engine oil, Mechanics & Industry, 17 1 104

(2016). https://doi.org/10.1051/meca/2015037

15. M. Habibullaha, H.H. Masjukia, M.A. Kalama, A.M. Ashrafula, M.A. Habibb, H.M. Mobaraka, Effect of biolubricant on tribological characteristics of steel, Procedia Engineering, 90 740–745 (2014). https://doi.org/10.1016/j.proeng.2014.11.807
16. M.K.A. Ali, H. Xianjun, R.F. Turkson, Z. Peng, X. Chen, Enhancing the thermophysical properties and tribological behaviour of engine oils using nanolubricant additives. R. Soc. Chem. Adv. 6, 77913–77924 (2016) 10.1039/C6RA10543B
17. H.H. Masjuki, M.G. Saifullah, M. Husnawan, M.S. Faizul, M.G. Shaaban, Flash Temperature Parameter Number Prediction Model by Design of Tribological Experiments for Basestock Mineral Oil Containing Palm Olein and Aminephosphate Additives. Proceedings of the World Tribology Congress III. USA 451-452, (2005). https://doi.org/10.1115/WTC2005-63193

Figures

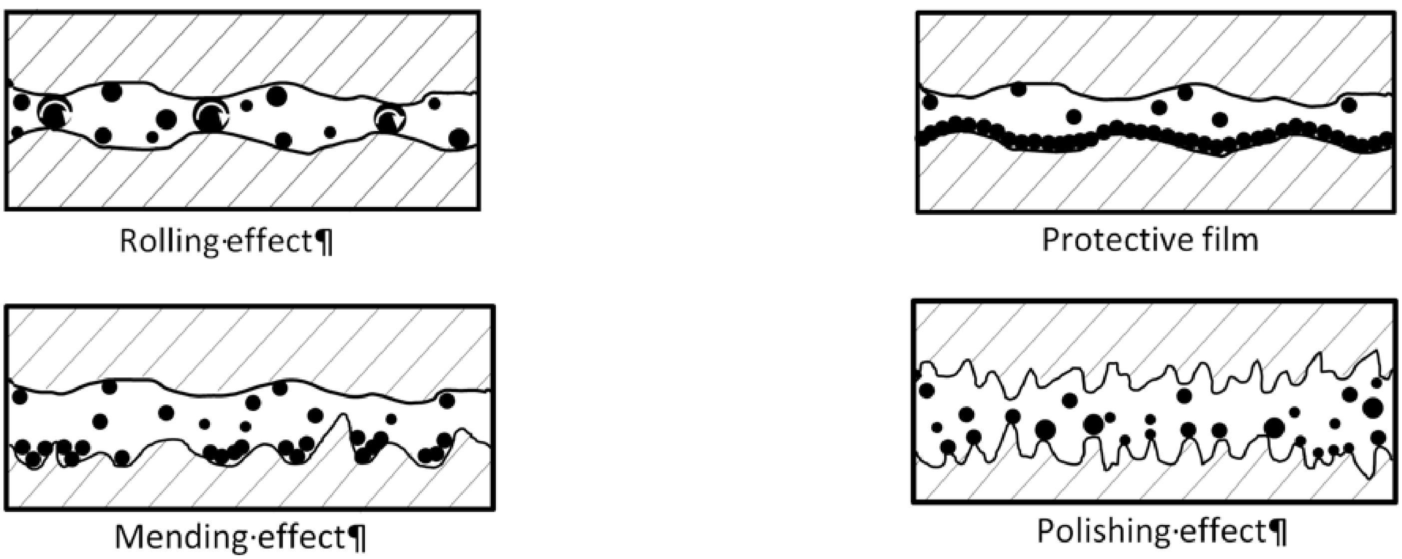

Figure 1

Lubricating mechanisms by NPs based lubricant [5]

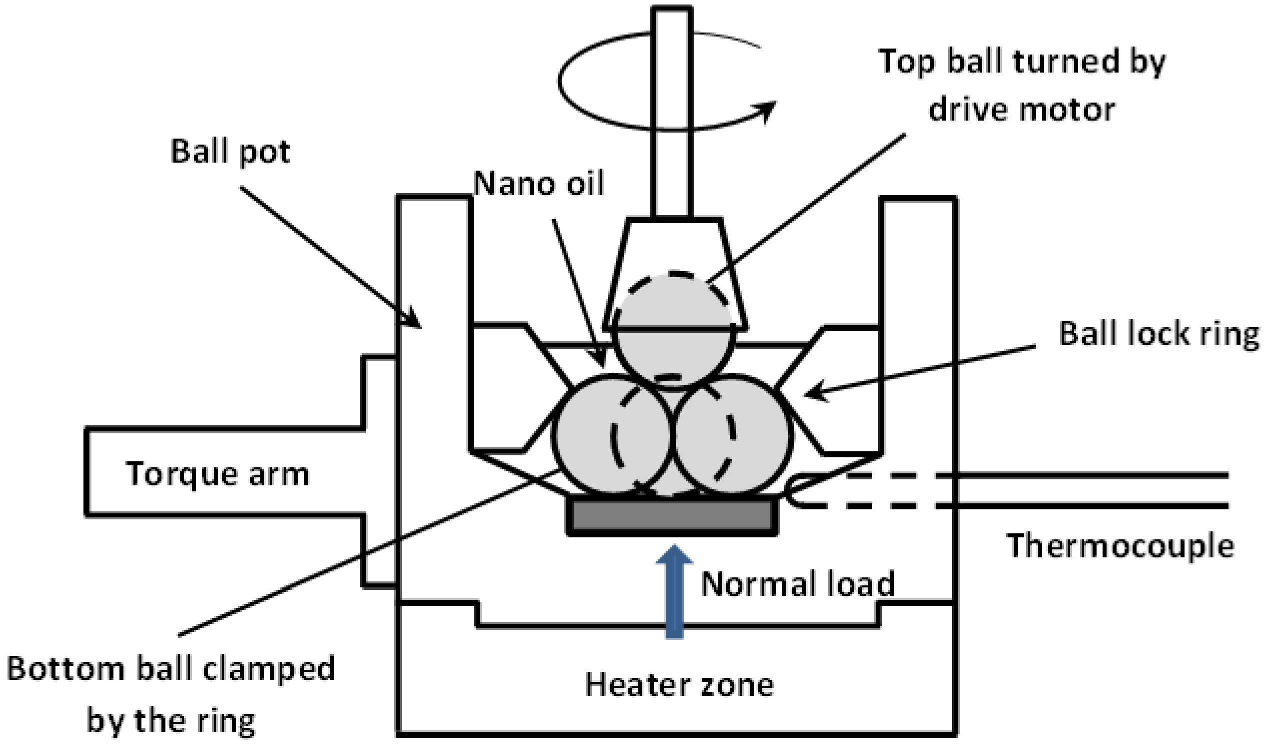

Figure 2

Schematic representation of four-ball tribometer

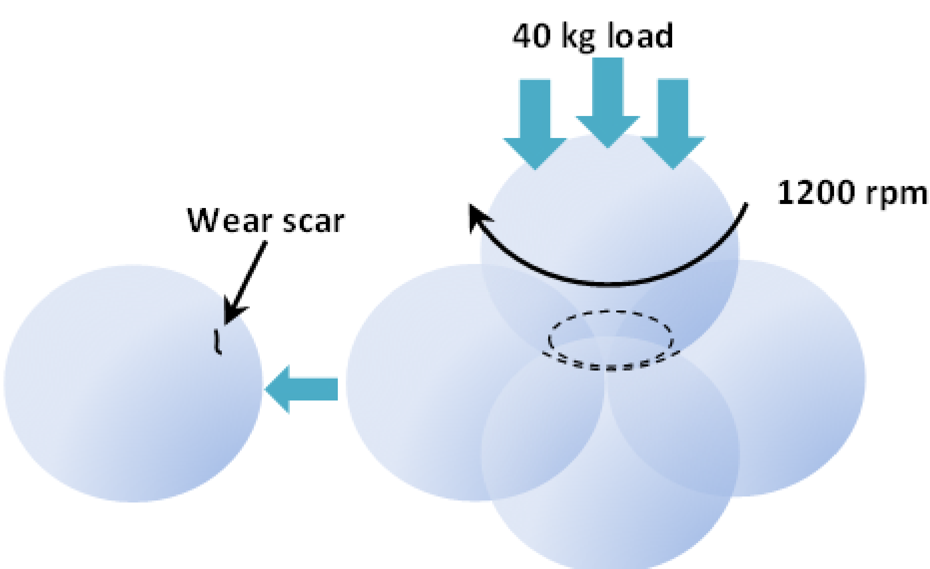

Figure 3

Four ball of Tribological system

Figure 4

SEM images of the ball wear scar map of pure base oil and 0.01, 0.25, 0.050 and 0.075 wt.% TiO_2 at RT after a 30-minute period of testing

Figure 5

SEM images of the ball wear scar map of pure base oil and 0.01, 0.25, 0.05 and 0.075 wt.% TiO_2 at 75°C after a 30-minute period of testing

Figure 6

Wear depth scar of lower balls at room temperature

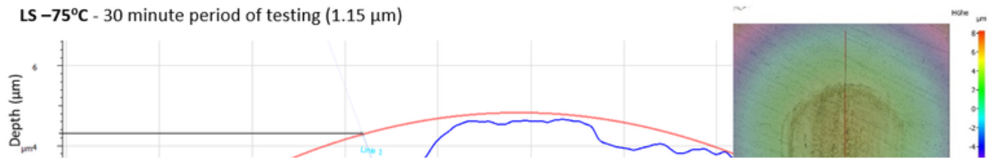

Figure 7

Wear depth scar of lower balls at 75°C

Figure 8

Ball wear volume for oils used in this work at different temperature

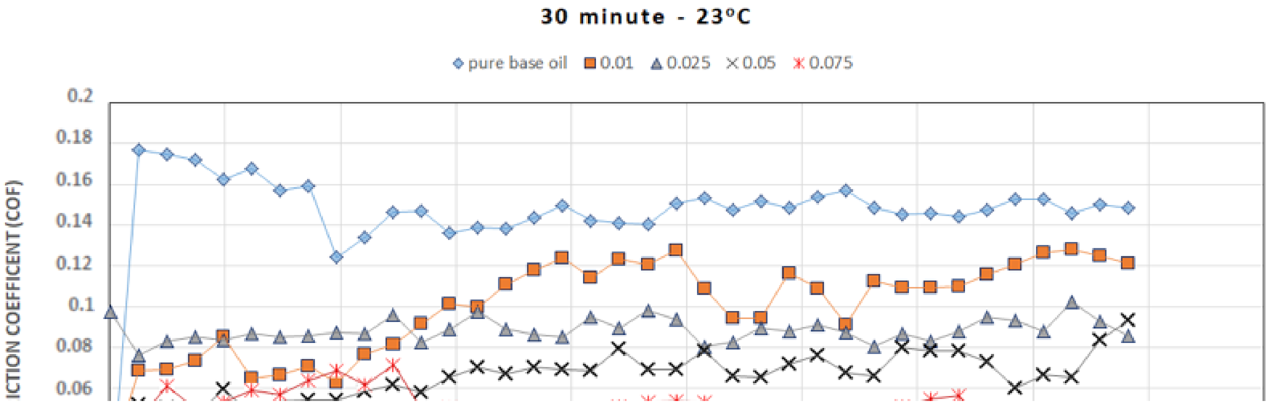

Figure 9

Coefficient of friction (COF) for different additive amounts of TiO_2 at RT (23°C) and 75°C

Figure 10

Average coefficient of friction (COF) for different additive amount of TiO_2 at RT (23^{o}C) and 75^{o}C and COF in steady state after rubbing effect

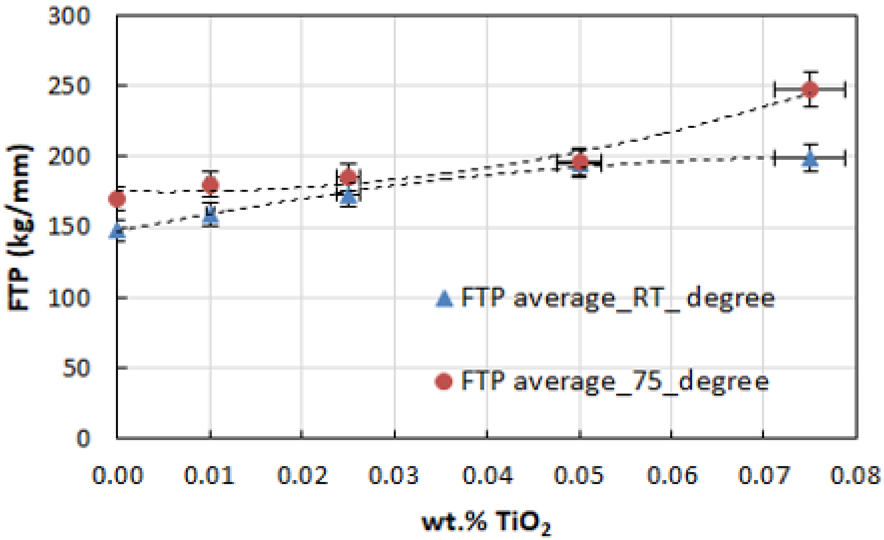

Figure 11

Plot of TiO_2 as a lubricant additive vs. flash temperature parameter FTP for different temperature