INVESTIGATION OF PHYSICOCHEMICAL AND TRIBOLOGICAL PROPERTIES OF TiO_2 NANO-LUBRICANT OIL OF DIFFERENT CONCENTRATIONS

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ABSTRACT

Nano-lubricants provide enhanced tribological properties in several applications like machines and engines. The presence of nanoparticles in the lubricating oil effects its wear, friction, thermal, chemical and physical properties in many ways. This article reports effect of TiO_2 nanoparticles suspended in servo system lubricating oil prepared by sonication process without adding any surfactant. Four different volume concentrations (0.2%, 0.4%, 0.6% and 0.8%) of TiO_2 nanoparticles in the base lubricating oil are used for analysis. Calorific value, flash point, viscosity are the physicochemical properties of the TiO_2 nano-lubricant investigated at different Volume Concentrations (VC). Wear scar diameter and coefficient of friction are the tribological properties analyzed for the prepared nano-lubricant at different VCs. Calorific value and flash point of the nano-lubricant was found to be decreasing with increasing VCs compared to base lubricant oil. Viscosity, on the other hand was almost same as the base lubricant oil for the proposed VCs. Wear scar diameter and friction coefficient was found to increase with increase in VC of TiO_2 nanoparticles in the lubricant oil. It is concluded that, to obtain better results agglomeration of nanoparticles has to be avoided which can be achieved with the use of surfactant.

Keywords: Nano-lubricant, tribological properties, friction coefficient, wear, viscosity

INTRODUCTION

To reduce friction and wear in engines, machines and other important devices involving sliding motion, many nanoparticles dispersed in the lubricating oil are being employed nowadays [1]–[4]. Nanoparticles based lubricant oils are generally coined as nano-lubricants. Various nanoparticles like TiO_2, SiO_2, Fe, Cu, LaF_3 etc., are used to analyze the tribological properties of the prepared nano-lubricant in the engines and machines [3],[5–10]. With the improvement in frictional properties, these nano-lubricants also have increased thermal conductivity [6][5], [11]–[17]. TiO_2 nanoparticles added to modify surface of liquid paraffin was reported to improve the load carrying capacity and reduction in wear [18].

With addition of ZrO_2 nanoparticles to lubricating oil, wear and friction performance changes and depending upon Volume Concentration (VC) of the nanoparticles gives less coefficient of friction than the lubricating oil [19]. Hexagonal boron nitride has good thermal conductivity, stability and frictional properties having nano and micro size particles of boron nitride [20–22].

Nanoparticles in lubricant have shown promising effect on tribological properties. When poly-alpha-olefin oil was mixed with nano onions, the nano-lubricant gave good anti-wear properties and it was observed that it gives better than graphite [12], [23]. Many research works are reported using TiO_2 nanoparticle as coating material and composite reinforcement to improve tribological properties. The nanoparticle diameter and size has a considerable effect on the behavior of the nano-lubricant [24]–[26]. Pottuz et al., studied wear and friction properties of WS_2 nanoparticles for lubrication and found drastic reduction in friction coefficient [27]. Lee et al., analyzed graphite nano-lubricants and concluded that wear and friction of the lubricant reduces considerably [28]. Wu et al., used TiO_2 nanoparticles in ethylene glycol and found gelation on the engine component surface. They changed the base oil to paraffin oil and found that smaller size nanoparticles of TiO_2 improves tribological properties. But, the nanoparticle size is limited below which it cannot be used in paraffin oil, whereas in ethylene glycol it can be used [2]. Jiao et al., prepared Al_2O_3/SiC composite nano-lubricants and found that they have reduced friction coefficient than pure Al_2O_3 and SiC nanoparticles [29]. 50% ZnO and Al_2O_3 nanofluid were prepared using deionized water and analyzed for its wear and friction properties and observed great reduction in these properties [3]. Sabareesh et al., used TiO_2 nanoparticle to study mineral oil lubricant's thermophysical properties. They found an overall improvement in COP of the refrigeration system due to use of the nano-lubricant based on TiO_2 [30].

We see that several investigations are carried out using different nanoparticles of different sizes and different VCs to reduce wear and friction properties of the lubricant. Even though TiO_2 based nano-lubricants are synthesized and analyzed for their tribological properties as reported in many works [2], [9], [18], [19], [24]–[26], [31]. But, no work is reported on analysis of any kind of chemical properties of TiO_2 based nano-lubricants. Along with this, no work is reported for different VC of TiO_2 in lubricant used for servo system. Hence this work is motivated to analyze the physicochemical properties of the TiO_2 based nano-lubricant and check the wear and friction characteristics for different VCs of 0.2%, 0.4%, 0.6% and 0.8% and comparison is made with the base lubricant (Servo system 68 oil) that is with 0 % VC of TiO_2 nanoparticle.

MATERIALS AND METHODS

Nano-lubricant preparation

The nanoparticles used in this study is TiO_2 with an average size of 30 nm to 40 nm. The servo system 68 oil (lubricant) was used as the base fluid for the present work and was purchased from Indian Oil Corporation Limited. It has a grade of ISO VG 68 and meets IS 10522-1983 specification. It provides long service life due to excellent resistance to oxidation, rust, corrosion and foam formation. The nano-lubricant was prepared by mechanical stirring and sonication method. The stirring was done in order to disperse the nanoparticles uniformly in the oil. The stirring was done by magnetic stirrer for 5 minutes. The standard ultrasonic cleaner was used for sonication. The bath temperature was set to 50 ^{o}C and it was maintained by changing the water for every new sample prepared. The sonification was done for 1.5 hours with a break of 5 minutes after every 15 minutes of pulse time. This was done in order to sonicate the lubricant oil without any change in physical properties due to increase in temperature of the bath. The following are the specifications mentioned in Table 1, of the ultrasonic cleaner used.

Table 1. Specification of the ultrasonic cleaner

Maximum power output	600 W
Operating frequency	20 kHz
Input	110 V AC @ 10 Amps
Programmable timer	1 s to 1 hr

Following the above method five samples were prepared with Volume Concentration (VC) of nanoparticles being 0%, 0.2%, 0.4%, 0.6% and 0.8% respectively in plastic containers. The nano-lubricant before and after sonification can be seen in Figure 1.

Figure 1. Ultrasonic cleaner and lubricant before and after sonication

Measurement of calorific value of the nano-lubricant

Bomb calorimeter is the commonly used instrument to find the calorific value of fuel or the lubricant. The specifications of the bomb calorimeter are also mentioned in Table 2.

Table 2. Specifications of Bomb Calorimeter

Specification	Details
Working Principle:	Iso-Thermal
Standards:	BS 1016: Part 5:1967 IS: 1359–1959 IP 12/63T
Experiment Duration:	10 - 15 min
Combustion Bomb Make:	SS 316
Jacket Type:	PUF Insulated SS Jacket
Temperature Resolution:	0.01 °C
Temperature Indicator:	Thermocouple based Digital Temperature Indicator
Bomb Firing:	Automatic

The heat energy measured in a bomb calorimeter may be expressed either as calories (cal), British thermal units (Btu) or Joules (J), with the International Steam Table calorie as the basic unit in this system. Heats of combustion as determined in an oxygen bomb calorimeter are measured by a substitution procedure in which the heat obtained from the sample is compared with the heat obtained from combustion of a similar amount of benzoic acid or other standardizing material whose calorific value is known. The construction and formulation is not discussed in detail since it is well documented in the literature [32–33].

The following Equation 1 is used to find the calorific value of the prepared TiO_2 nano-lubricant:

$$\text{Calorific value, } CV = \frac{\Delta T \times 2936}{g} \tag{1}$$

Where CV = Calorific value of the sample (cal/gm), ΔT = Change in temperature of the sample before and after ignition (^oC), 2936 = Energy equivalent of the calorimeter (cal/^oC) and g = Weight of the sample taken in the crucible (gm)

Measurement of flash point of the nano-lubricant

Employing standard (ASTM D92) flash point apparatus (closed cup type) used in the present study. This apparatus has accessories to measure low range temperature (IP 15C) and high range temperature (IP 16C). The assembly rests in air bath, which is covered, with dome shape metal top. The cup is fitted with insulated handle and locking arrangement near cup flange. The assembly is kept on round shaped electric heater with Energy regulator temperature control. Suitable for operation on 220 Volts 50 cycles AC. The cup is cleaned and the sample is placed in it and closed. The test flame is introduced in to the oil vapour for every 1 ^oC rise in temperature and when the test flame causes a distinct flame in interior cup the temperature is noted down.

Measurement of viscosity of the nano-lubricant

The typical Redwood viscometer (temperature range 30 ^oC to 85 ^oC and upper limit of viscosity 2000 sec following ASTM D446 standards) was used to find the viscosity of the lubricating oil. It consists of an oil cup which holds the test sample. The bottom of the cup is fitted with polished-agate discharge tube containing an orifice of specified dimension. The oil cup is surrounded by water bath in order to adjust the oil temperature. A standard flask is placed below the orifice to receive the oil. The water bath is heated which in turn heats the oil and the oil is made to fall in the flask drop wise. The time required to fill the flask is noted and the viscosity is found. Equations 2 and 3 were used to find the kinematic viscosity:

$$\nu = (0.26T - \frac{179}{T}) \text{ if T < 100 sec} \qquad (2)$$

$$\nu = (0.247T - \frac{50}{T}) \text{ if T > 100 sec} \qquad (3)$$

Where ν = Kinematic viscosity (cSt) and T = Time for the flow of 50 ml of sample oil (sec.)

Measurement of tribological properties of the nano-lubricant

The Four Ball-Tester is employed to measure the Anti-Wear (AW) and Extreme Pressure (EP) properties of the nano-lubricant. The point contact interface is obtained by rotating a 12.7 mm diameter steel ball under load against three stationary steel balls immersed in the lubricant. The speed of rotation, normal load, and temperature can be adjusted in accordance with published ASTM standards. To evaluate the anti-wear characteristics of lubricants, the subsequence wear scar diameters on the balls is measured. To evaluate the Extreme-Pressure (load-carrying) capacity of lubricants, the normal load at which welding occurs at the contact interface, is measured. In the present work wear characteristics are found using ASTM D 4172 standard. The following Figure 2 shows the Four-Ball tester and various parts of it respectively.

Three ½ in. (12.7 mm) diameter steel balls are clamped together and covered with the lubricant to be evaluated. A fourth ½ in. diameter steel ball, referred to as the top ball, is pressed with a force of 40 kgf (392 N) into the cavity formed by the three clamped balls for three-point contact. Then the top ball is rotated at 1200 rpm for 60 min. Lubricants are compared by using the average size of the scar diameters worn on the three lower clamped balls. The test stops automatically after completing of test duration or after weld. When oil temperature reaches room temperature, the scar produced on the three balls are marked and measured on the microscope. Two measurements on each of the three scars, one along the striations and other across the striations is taken and the average of the six readings is recorded as scar diameter.

Figure 2. Four-ball tester machine and its various parts

Table 3. Specifications of Four Ball tester

Parameter	Specification
Rotational speed	3000 rpm (max)
Test Load	Up to 10000 N or 1000 kgF
Temperature	Ambient to 100 °C
Standards	ASTM D 4172 ASTM D 2783

RESULTS AND DISCUSSION

The physicochemical properties such as calorific value, flash point and kinematic viscosity of the TiO_2 based nano-lubricant with different VCs of TiO_2 were found using the equipment's mentioned in the previous section. These properties are important in understanding the behavior of the oil during lubrication where due to friction heat is generated. The tribological properties like wear scar diameter and friction coefficient were found using the four ball tester equipment adopting the described procedure previously. The base lubricant oil (0% VC) was also tested for comparing the values with the prepared nano-lubricant without any surfactant of VCs (0.2%, 0.4%, 0.6% and 0.8%). The following are the results obtained during the study.

Calorific value

The calorific value of the Servo system 68 oil (lubricant) with various VCs of TiO_2 was found using Bomb Calorimeter (ASTM D5865). The results obtained are plotted as graph as shown in Figure 3. It is observed that the calorific value of the nano-lubricant decreased drastically when compared to base oil, and as the concentration of TiO_2 increased the reduction in calorific value is not that significant. We can see that for 0.2% VC of TiO_2 upto 10% reduction in calorific value is obtained while for further 0.2% addition of

TiO_2 nanoparticles reduced the calorific value by just 1.8%. And further addition of nanoparticles is similarly causing very less reduction in calorific value of the nano-lubricant. This reduction in the calorific value is due to the presence of the nanoparticles which will do not participate in combustion. We have to further see what effect will be there on other properties in order to conclude the use of addition of TiO_2 particles.

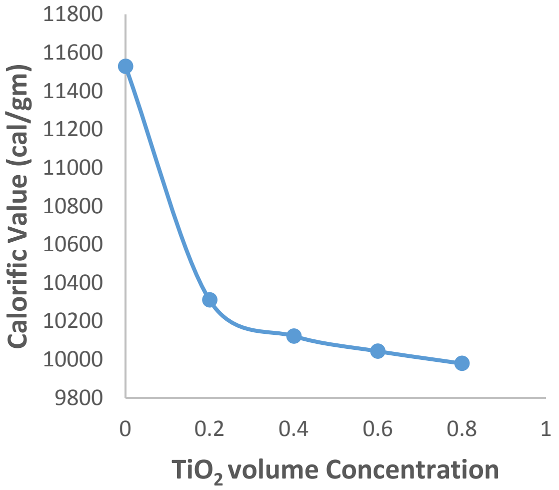

Figure 3. Reduction in calorific value of TiO_2 nano-lubricant for different VC

Flash point

The flash point of the Servo system 68 oil (lubricant) with various TiO_2 nanoparticle VCs along with the base oil is found. The results are shown in Figure 4. The flash point characteristics is found similar to that of calorific value which decreased along with the addition of nanoparticles and tends to be stabilized after 0.6% concentration. The flash point is an important parameter in tribological application which will decide the extreme temperature limits for the application of the lubricant. The flash point of the nano-lubricant decreased by about 30 °C (for 0.2% concentration) compared to the base oil which is not desirable. The flash point characteristics can be studied with addition of surfactants in future to see whether an improvement in results are obtained.

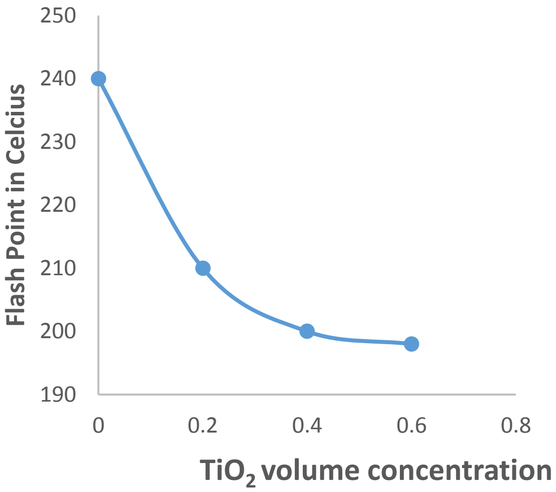

Figure 4. Reduction in flash point of TiO_2 nano-lubricant for different VC

Kinematic viscosity

The kinematic viscosity of the nano-lubricant was found using Redwood Viscometer. The test was conducted at three different temperatures i.e., 32 °C (room temp.), 40 °C, 50 °C. The Figure 5 shows the viscosity of the Servo system 68 oil (lubricant) with various TiO_2 nanoparticle concentrations. It is evident from the graph that the viscosity of the nano-lubricant as well as the base oil does not vary much with temperature. It is found that the highest viscosity at room temperature is for nano-lubricant with 0.8% TiO_2 concentration (100.61 cSt) which is due to high concentration of nanoparticles, and since viscosity reduces as temperature increases for liquids, it can be seen that there is a reduction in kinematic viscosity of the samples at 40 °C and 50 °C respectively. Kinematic viscosity in acceptance with the base oil may be obtained with addition of surfactant which will disperse the nanoparticles more evenly without agglomeration.

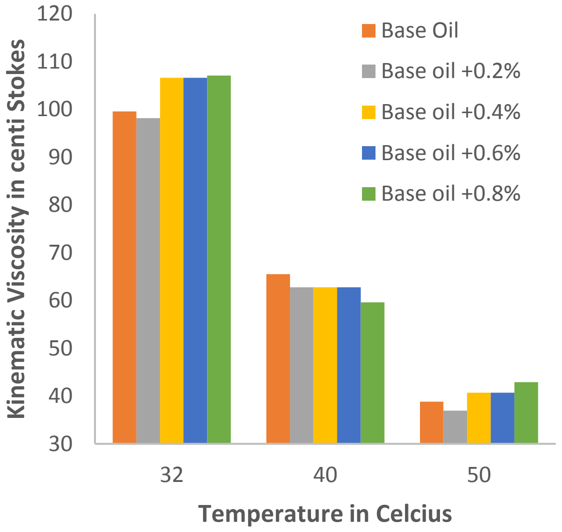

Figure 5. Variation of Kinematic viscosity with temperature of TiO_2 nano-lubricant for different VCs at different temperatures

Wear scar diameter and co-efficient of friction

The wear scar diameter of the balls used in Four-Ball tester was measured using a microscope. The results obtained for different VCs of nanoparticles of TiO_2 are shown in Figure 6.

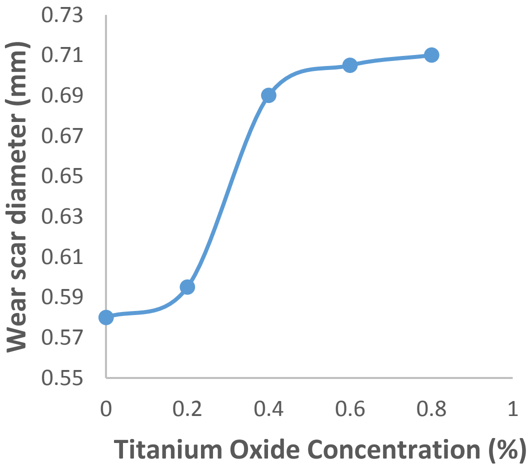

Figure 6. Wear scar diameter of TiO_2 nano-lubricant for different VC

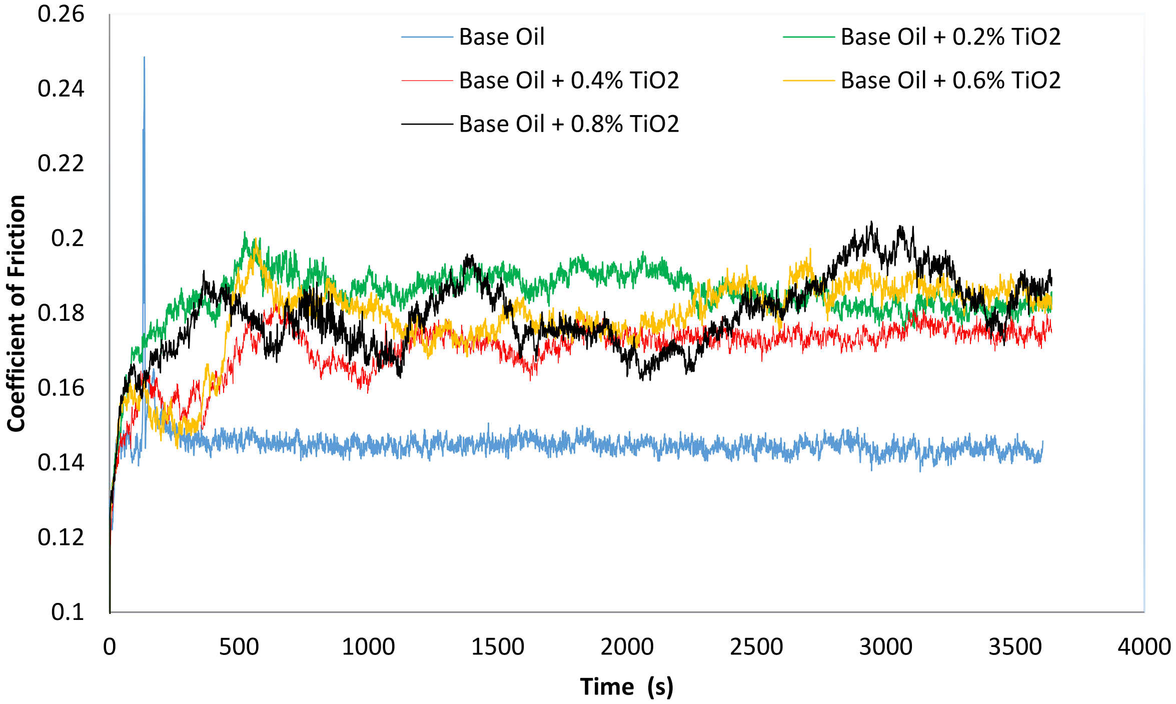

Figure 7. Coefficient of Friction as a function of time of TiO_2 nano-lubricant for different VC

The friction co-efficient of the wear in the balls used was found for every 1 s by keeping load at 40 kg, speed at 1200 rpm and temperature at 75 °C constant. The Figure 7 shows the friction co-efficient as a function of time. It is evident from the plots that the wear scar diameter and coefficient of friction increased with the increase concentration of the nanoparticles. This increase caused is due to agglomeration of the nanoparticles. The nanoparticles agglomerated due to the absence of a dispersant or the surfactant. The presence of the dispersant would disperse the nanoparticles uniformly and evenly in the oil. Also the TiO_2 nanoparticles used in this study tend to coagulate in the oil leading to the poor wear properties. Another main reason for the agglomeration is the pulse and break time of the sonication process. For better results, the pulse and break time must be 5 minutes each i.e., every 5 minutes the sonicator should be put off and should be restarted after 5 minutes.

CONCLUSIONS

In this work, an experimental investigation of physicochemical and tribological properties of prepared TiO_2 nano-lubricant is carried out. Four different volume concentrations of TiO_2 nanoparticles are employed and compared the properties with base lubricant oil (servo system oil). The nano-lubricant was prepared by one step method and no surfactant was used during ultrasonication. The following conclusions are drawn from the analysis:

- The calorific value and flash point of the base lubricant oil compared with TiO_2 nano-lubricant decreased with increase in volume concentration.
- The kinematic viscosity of the base lubricant oil and the TiO_2 nano-lubricant at 40 °C (at standard experimental temp.) was almost same. There was no much difference in the viscosity at higher temperatures comparatively.
- The wear and friction properties of TiO_2 nano-lubricant found using Four-ball tester showed poor results in wear resistance.
- It is concluded that, the main reason behind the decrease in these properties is due to agglomeration of TiO_2 nanoparticles as any surfactant was not used during preparation of the nano-lubricant. Hence, surfactant will definitely help in uniform distribution of nanoparticles and thereby improving the above properties. The results obtained in this study are not acceptable from chemical and tribological point of view.

Scope for Future Work

- Further study can be made on the extreme pressure characteristics of the nano-lubricant.
- Study can be made with the addition of the dispersant or the surfactant.
- Also optimum nanoparticle as well as the dispersant to be added in the oil in order to obtain better performance.
- Different oils and nanoparticles can be studied with the same procedure in order to improve the wear resistance properties.
- Further study can be made on the types of TiO_2 nanoparticles to be used i.e., anaphase and rutile in order to compare the lubrication performance.

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