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Impact of Nano-Gel of titanium dioxide Additive on Base Oil Properties Produced in Iraqi Refineries

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Abstract
The researchers are doing their best to find the best methods and techniques to improve the lubricating oils specifications. In addition to trying to produce environmentally friendly and low cost lubricating oils In the present research a Nano-gel of titanium dioxide have been studied to be added to mineral base oil produced by Al- doura Iraqi refinery at volume percentage of (0.5%, 0.75%, 1%, 1.5%, 2%, and 3%), and investigate its effects on base oil properties as well as its tribological performance. It revealed slight effects on viscosity index and density while an obvious rising in pour point and flash point. Remarkable reduction was in specific wear rate and coefficient of friction results, which import a friction reducing in machine parts.

Keywords: Base oil, Nano-gel, Titanium dioxide, Tribological performance.

تأثير المضافات النانوية على مواصفات زيوت الأساس المنتجة في المصافي العراقية

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الخلاصة
يبذل الباحثون قصارى جهدهم لأعداد أفضل الطرائق و التقنيات لتحسين مواصفات زيوت التزييت،اضافة لجعلها زيوت صديقة للبيئة وغير مكلفة اقتصاديا. في البحث الحالي تمت دراسة اضافة الجل النانوي لثنائي اوكسيد التيتانيوم الى زيت الاساس المنتج في مصفى الدورة العراقي وعند نسب مئوية حجمية (0.5%، 0.75%، 1%، 1.5 %، 2%،3%) ، و دراسة تأثيرها على مواصفات زيت الأساس و على أداء البري لزيت الأساس. لقد أظهر البحث تأثير طفيف على معامل اللزوجة و الكثافة، بينما لوحظ ارتفاع واضح في درجة الانسكاب و درجة الوميض. وظهر انخفاض واضح في نتائج معدل البري النسبي ومعامل الاحتكاك والتي هي بالتالي ستقلل من احتكاك أجزاء المحرك.

1. Introduction

Lubrication is described as any process that has the ability to reduce the friction in moving contacts. This reduction can be achieved by a solid or liquid material called lubricant [1]. Basically, the lubricant consists of base oil which act as a carrier of additives, while the function of additives is to enhance an existing property of the base lubricant or to add a new property [2]. Lubricating oils according to Durrani [3] are used to protect the rubbing surfaces as well as promote easier motion for the connected parts and furthermore works as a medium to remove excessive temperature.

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The revolution of nanomaterials in many industries dealing with various applications since they possess unique specification in comparison with the same mass materials at the microscale, owing to their small size and exceptional surface aria per unit volume.

Nanotechnology involves; manufacture, processing, and application of nanomaterials that are less than100 nm in size [4, 5]. Nano fluid expression refers to a base fluid that has already been mixed with nanoparticles in order to enhance its quality. Lubricating oil can act as the base fluid among a list of different liquids [6, 7].

Nano fluid lubricants are employed in several industries and for different applications. It shows low sensitivity to temperature and finite tribochemical reactions [8]. Moreover, nanoparticles as additives have the ability to create a layer of thin film in the rubbing surface in order to reduce the friction coefficient and play an important role in self-repairing in which filling and repairing the friction surface to a certain limit[7,9,10].

In fact, approximately 48% of the energy developed can be saved during an operation in a specific engine while friction is reduced [11]. The most famous nanomaterials that are qualified to be used as additives in lubricants are metal oxides in about 26%, as shown in Figure-1[12].

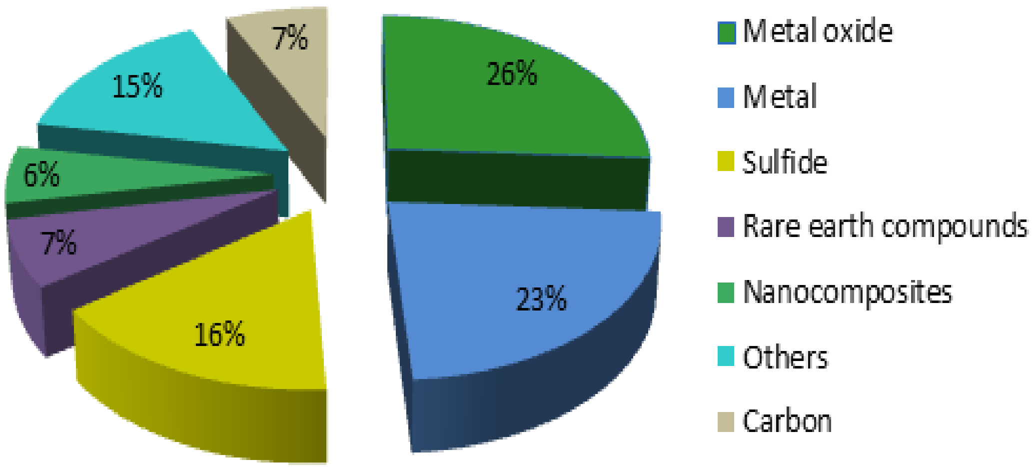

Figure 1-The well-known nano materials percentages that used as additives in lubricating oils [12].

Among these Nano metal oxides additives; titanium dioxide (TiO_2) that can be distinguished by: Good performance on anti-oxidant characteristics, relatively low toxicity, non-volatile, pleasant odor, stability of its chemical structure, optical, and electrical properties [13,14, 15].
There are three forms of TiO_2: Brookite, Anatase, and Rutile. Anatase type is the preferred one because of its high specific area, good features in coating, and superior advantage in anticorrosion behavior and self-healing effects [16]. While rutile type applications are in the same fields but with lower reverberation, as well as the rutile enter in the cement mixture as a photo motivator to get a superior glossy surface [17, 18]. So, the major aims of the present research is:

- To study the impact of using nanoparticles, particularly Nano-gel of Titanium dioxide, by blending it with mineral base oil 60 produced in Al- Doura Iraqi refinery to improve the lubricant specification, especially, its tribology performance
- Achieving the goal of having an advanced and low cost lubricating oil re without any negative effects on biological life, by using the Green chemistry, meaning: low concentrations of Nano materials instead of high concentrations of harmful chemical materials which are consider an environmental pollutant.
- Investigatingand improving Iraqi mineral base oils.

2. Materials and methods

2.1. Materials

Several materials was employed in this work to manufacture the nanomaterial; titanium chloride ($TiCl_3$, 99.0%, BDH), Hydrochloric acid (HCl, 33%, Aldrich), Acetic acid (CH_3COOH, 99.8%, Aldrich), and Hydrogen Peroxide (H_2O_2, 35 wt. % aqueous solution, Aldrich). Mineral base oil (60) (from Al-Doura refinery, Baghdad, Iraq) was used in the present study. Table-1 summarize the standard methods of the present work tests and the physical properties of the mineral base oil. In the tribological tests the disks were manufactured of stainless steel and the pin material was formed by an aluminum alloy. also (99.8%, Aldrich) has also been used as a clean material in wear experiments.

Table 1-Standard testing methods of lubricating oils

Property	Viscosity (cSt) at 40◦c	Viscosity (cSt)at 100◦c	Viscosity Index	Pour point (◦c)	Flash point (◦c)	Density (g/ml) at 15.6◦c
Testing methods	D445	D445	D2270-93	D97-02	D92	D941-5
Mineral Base Oil(60)	62.99	8.413	103.6	-11	222	0.875

2.2. Preparation of Nano fluid

Preparation method of the nanomaterial was performed according to the method of Zhangwen e al. [19]. The perceptible Nano gel has been employed in the present work experimental procedure by adding different amounts of the prepared Nano gel (0.5, 0.75, 1, 1.5, 2, and 3 vol. %) to the base oil with the help of an ultrasonic technique (SONICS/ Vibra cell) associated with cooling bath . The operation conditions of the process were 40°C for 15 h (10 sec ON: 5 sec OFF) at 750 w and 20 KHz with 40% amplitude to ensure a homogenous and superior dispersion media without any agglomeration of the Nano particles, followed by heating to 95°C while stirring for 10 min.

2.3. Physical properties of mineral base oil

The most important and essential parameters of mineral base oil are the viscosity and viscosity index. Where the viscosity ensures a hydrodynamic lubrication with a sufficient film formation, but not to the limits as to cause increase of friction losses in the oil. To measure the kinematic viscosity at 40°C and 100°C a viscometer (HVV481/UBBELOHD) (Herzo/ Germany) was used. The viscosity index would be determined by Dean&Devis equations (particular for oils of viscosity index of 100 and greater) and its calculations according to ASTM (D 2270 – 93), as seen in equations (1) and (2):

$$VI = \left[\left((antilogN) - 1\right)/0.00715\right] + 100 \quad (1)$$

$$N = (logH - logU)/logY \quad (2)$$

Where Y represents the kinematic viscosity at 100°C of oil whose viscosity index is to be calculated, mm^2/s (cSt), H is the kinematic viscosity at 40°C of oil with a viscosity index 100 having the same kinematic viscosity at 100°C as the oil whose viscosity index is to be calculated mm^2/s (cSt), U is kinematic viscosity at 40°C of the oil whose viscosity index is to be calculated mm^2/s(cSt).

The viscosity index (VI) is an important property in the systems that operate over a wide range of temperature just as in automotive engine. In addition to viscosity and viscosity index, several physical properties of the nano fluid have been investigated; density test at (15.6)°C, flash point, and pour point using a measuring instrument (Koehler Instrument/ Germany). Table-1 demonstrate the standard methods of the present work tests.

2.4. Tribological performance

With a pin-on-disk tribometer(locally manufactured), the tribological performance was investigated, . The standard method test was according to ASTM G99. The pin holder of this instrument is connected to a vertical linear motion system and the disk is mounted on a precision spindle with a rotational speed about 950 rpm.

The operation conditions of tribological tests were:

- The applied load 30 N.
- TiO_2 nanoparticles of concentrations (0, 0.5, 0.75, 1, 1.5, 2, 3) vol. %.
- Sliding speed of 2 m/sec, sliding distance 960 m.
- All tests were carried out for a duration time of 8 min.
- The pins diameters were 1 cm and 2.5 cm in length.

Disc and pins were polished by a smoothing paper and cleaned with acetone and dried. The load was placed on the pin by the help of dead weight through pulley-string arrangement, and the lubricant about (1ml) placed between the pin and the disc, taking into account an equal thin film with full-scale lubricant coating of the disc in all tests. In order to compute the weight losses of the pin in each wear experiment, the pin was measured with an electronic weighing balance of accuracy of 0.1 mg. This procedure was repeated for all the tests. After converting weight losses to volume losses, the specific wear rate have been calculated by Equation (3), which is known as Archard equation.

$$W_S = \frac{\Delta V}{L \times d} \quad (3)$$

Where, W_S is the specific wear rate (m^2/N), ΔV is volume loss (m^3), L is load (N), and d is the sliding distance (m).

The coefficient of friction (μ) is plotted as a function of the Sommerfeld number (S) as seen in Equation(4) This curve is known as the Stribeck curve (Shigley&Mischke, 1996).

$$S = \frac{\eta \times N}{P} \quad (4)$$

Where, η is the dynamic viscosity of the lubricant in (mPa.s), N is the sliding speed (m/s), and P is the applied load in(N).

Stribeck curve allows the evaluation of the lubricant tribological performance in various lubrication conditions.

3. Results and Discussion

3.1. Characterization of TiO_2 nanoparticles

Titanium dioxide nanoparticles were prepared by the Sol-gel method. It was characterized by X-Ray diffraction (XRD) test, which revealed the existence of Rutile and Anatase forms as shown in Figure-2. The employed nano-gel was characterized by Atomic force microscopy (AFM), as shown in Figures (3&4) from which the size of TiO_2 nanoparticles was demonstreated to be about (6.76 nm).

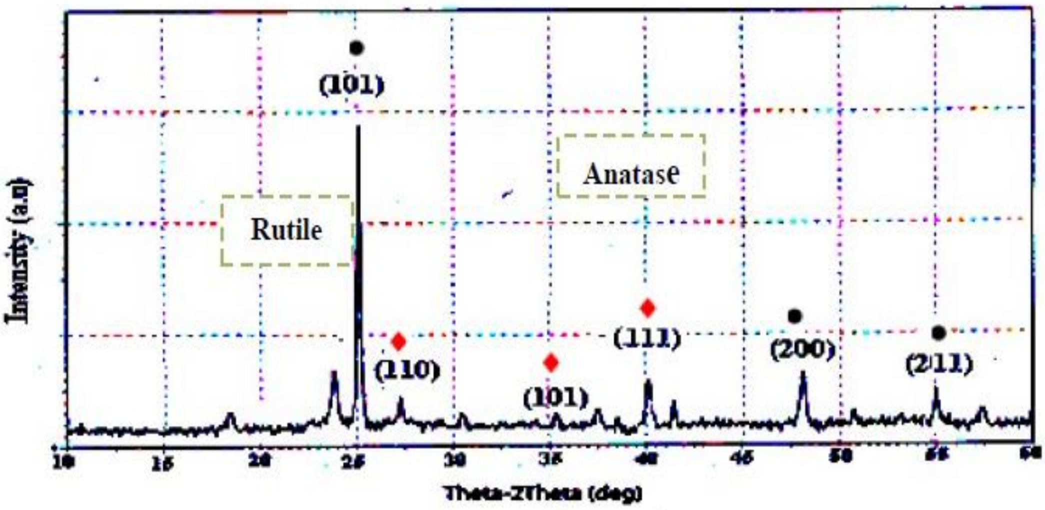

Figure 2-XRD spectrum of the prepared TiO_2 by sol-gel.

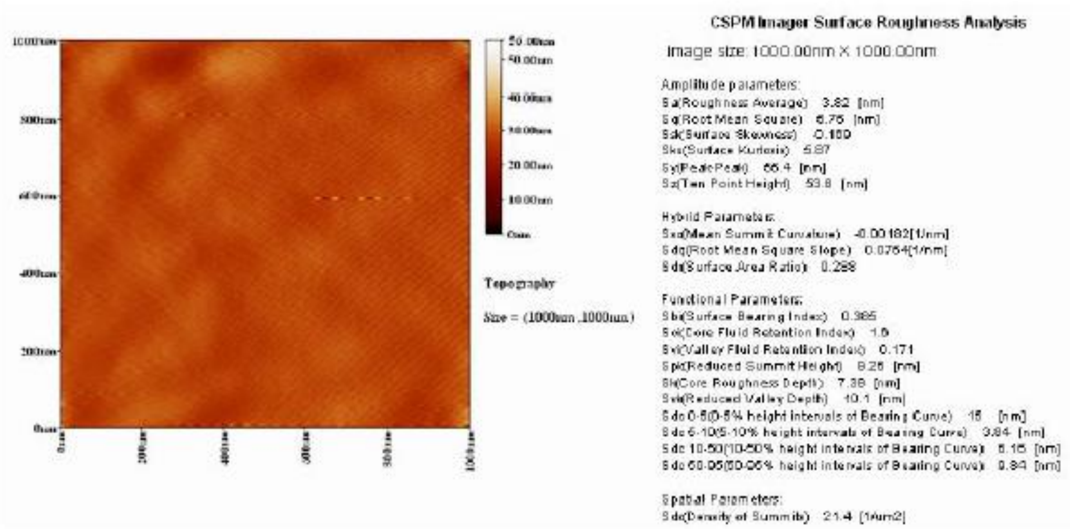

Figure 3- AFM image of Titanium dioxide nano-gel

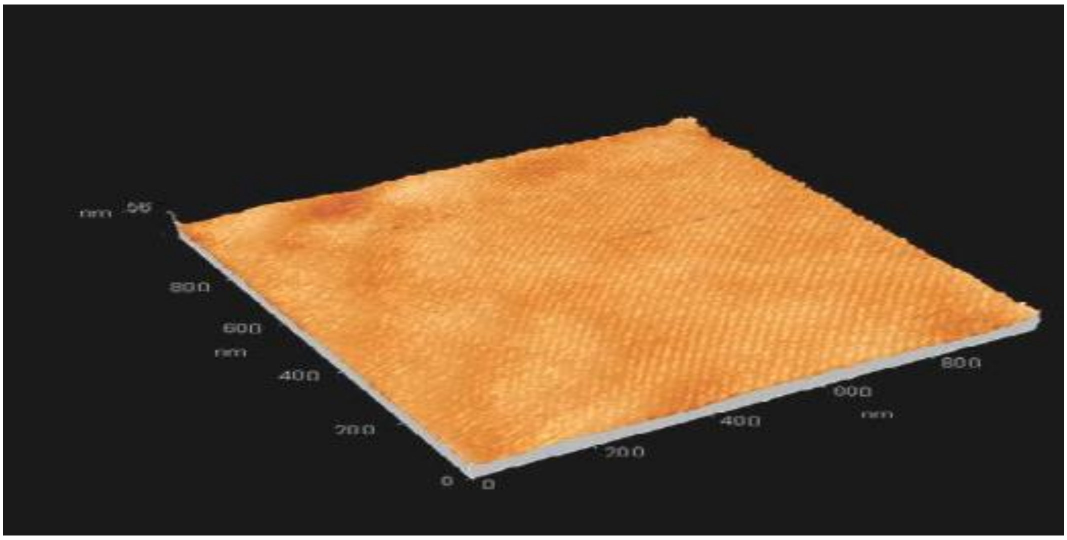

Figure 4-AFM image of Titanium dioxide nano-jel

3.2. Physical properties tests

In the present work , the viscosity was studied at 40°C and 100°C , viscosity index (VI), pour point, flash point and the density of the nano fluid as shown in Table-2. A negligible rise in density value at 3 vol. % can be noticed. This rise is because of the increase of nanomaterial concentration in the lubricating oil.

Table 2-Results of Nano fluid Properties

TiO_2 concentration with base oil (vol. %)	Pour point (◦c)	Flash point (◦c)	Density (g/ml) at 15.6(◦c)	Viscosity (cSt)		Viscosity Index (VI)
				At 40 (◦c)	At 100 (◦c)	
0	−11	222	0.875	62.99	8.413	103.6
0.5	−14	234	0.876	65.039	8.558	102.19
0.75	−16	235	0.878	65.262	8.579	102.25
1	−15	233	0.878	65.572	8.605	102.03
1.5	−15	233	0.878	65.076	8.544	101.74
2	−14	230	0.878	64.972	8.527	101.51
3	−13	227	0.879	64.950	8.519	101.39

Figure-5 shows the effect of TiO_2 nanoparticles concentration on VI of lubricating oil, which illustrate a slight decrease on VI as the concentration of TiO_2 increases. In spite of this increase, its magnitude is still accepted since it is still above 100. This indicates the existence of paraffinic contents hgh

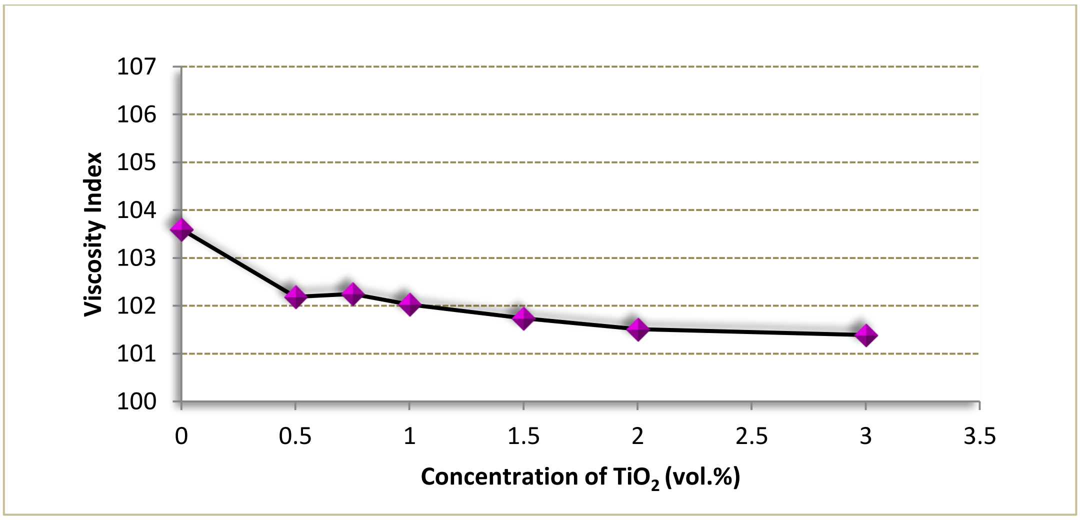

Figure 5-Effect of Nano TiO_2 concentration on Viscosity index.

Figure-6 indicates the effect of TiO_2 nanoparticles concentration on pour point values, revealing an increasing in pour point value, and the highest value was at the addition (0.75) vol. % of TiO_2 concentration. The behavior of flash point against the concentration of TiO_2 nanoparticles is as demonstrated in Figure-7, which was also an increasing in flash point values reaching the highest value at (0.75) vol. % nanoparticles concentration. After that, a gradual decrease reaching the lowest value at (3) vol. % concentration of TiO_2,

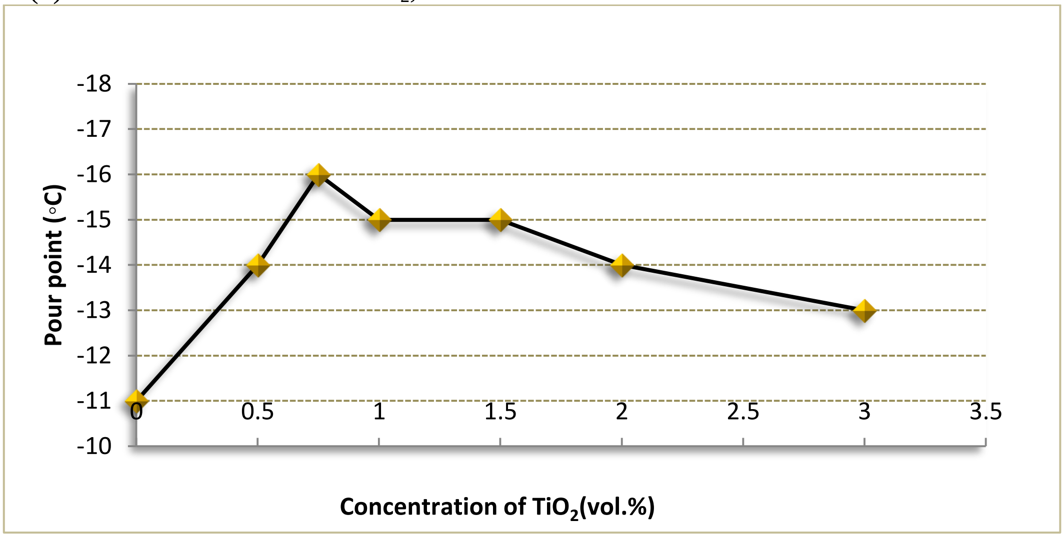

Figure 6-Effect of Nano TiO_2 concentration on pour point.

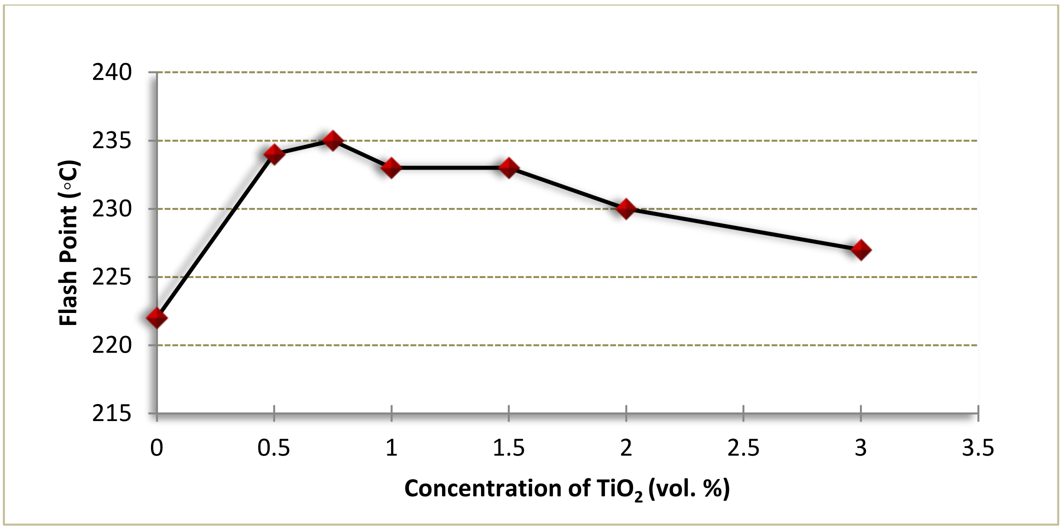

Figure 7-Effect of Nano TiO_2 concentration on flash point.

3.3. Wear test

Wear phenomena have occurred between the surface modified by TiO_2 nanoparticles and the metal surface during the sliding movement of the pin-on-disk tribometer, as shown in Table-3. A decrease in weight loss for pins can be noticed whenever there is an increase of TiO_2 nanoparticles concentration. The minimum value of weight loss was at (2) vol. % concentration of TiO_2 nanoparticles.

Table 3-Wear test results (at load (30 N)).

Nano material concentration with base oil (vol. %)	Initial Pin Weight (g)	Final Pin Weight (g)	Weight Loss (g)	Efficiency%
0	6.2720	6.2600	0.0120	0
0.5	6.2528	6.2420	0.0108	10
0.75	6.2351	6.2247	0.0104	13.33
1	6.2181	6.2083	0.0098	18
1.5	6.2022	6.1930	0.0092	23.3
2	6.1873	6.1790	0.0083	30.8
3	6.1726	6.1629	0.0097	19.16

Figure-8 shows the reduction in specific wear rate against the rising in concentrations of nano material, which gives about 30.8% efficiency at (2) vol. % nanoparticle concentrations as shown in Figure-9. The relation between the coefficient of friction and the concentration of Nano TiO_2 in lubricant has been shown in Figure-10.

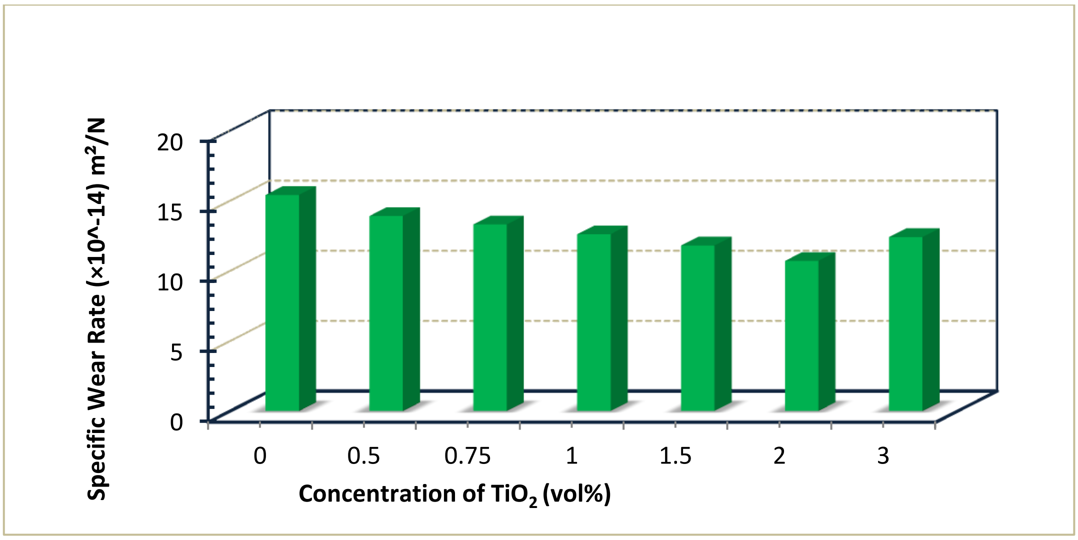

Figure 8-Effect of concentrations of Nano TiO_2 on specific wear rate

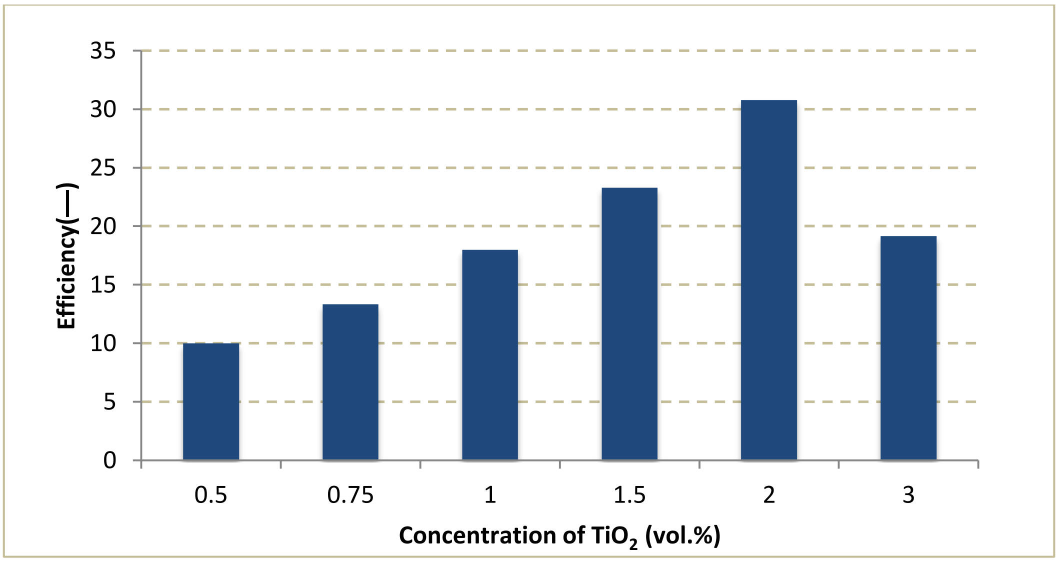

Figure 9-Efficiency against the concentrations of Nano TiO_2

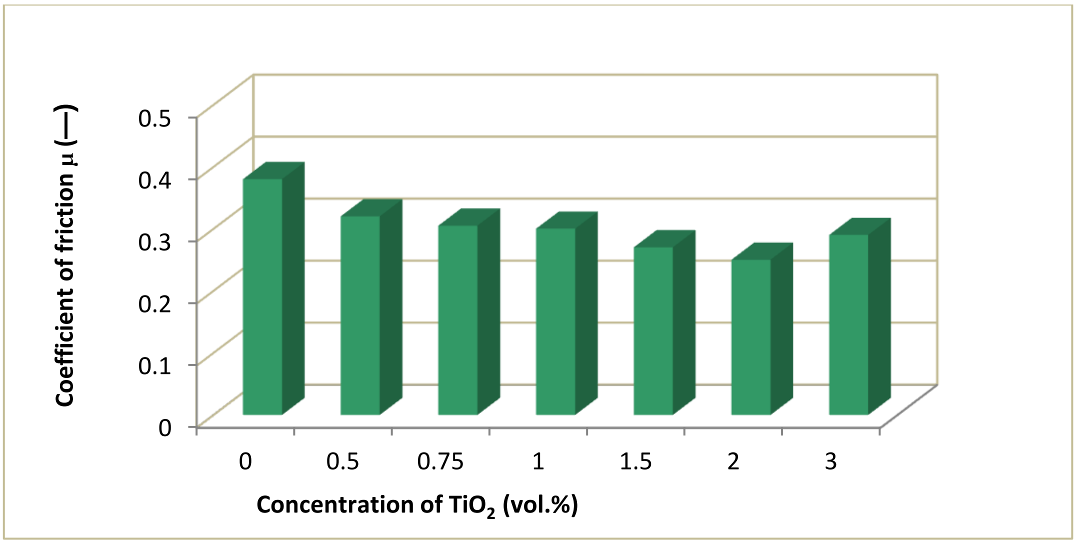

Figure 10-Effect of Nano TiO_2 concentration on coefficient of friction

It shows a decrease in the coefficient of friction. The lowest value was at 2 vol. %, but at the highest concentration 3 vol. %. The tribological performance including the coefficient of friction and the wear results were observed to be reduced. This is due to the high volume concentration that brought a worsening in the tribological performance of the lubricant.

4. Conclusions

1. Applying a Nano-gel of titanium dioxide in the mineral base oil manifested an improvement in several properties of the resultant nano fluid.
2. Slight reduction in viscosity index was noticed, in spite of this the values are still acceptable.
3. The addition of nano-gel titanium dioxide has revealed a positive effect on pour point and flash point results.
4. An obvious improvement on the coefficient of friction and specific wear rate after the addition of Nano-gel titanium dioxide was noticed with a good efficiency results.

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