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Rheological and Thermal Properties of Lubricating Oil Enhanced by the Effect of CuO and TiO_2 Nano-Additives

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Abstract

The specifications of lubricating oil are fundamentally the final product of materials that have been added for producing the desired properties. In this research, spherical nanoparticles copper oxide (CuO) and titanium oxides (TiO_2) are added to SAE 15W40 engine oil to study the thermal conductivity, stability, viscosity of nano-lubricants, which are prepared at different concentrations of 0.1%, 0.2%, 0.5%, and 1% by weight, and also their pour point, and flash point as five quality parameters. The obtained results show that CuO nanoparticles in all cases, give the best functionality and effect on engine oil with respect to TiO_2. With 0.1 wt. % concentration, the thermal conductivity of CuO/oil and TiO_2/oil increased by 7.27% and 4.54%, respectively. In the same time, the flash point of them increased by 12.62% and 9.3%, respectively in comparison with parent oil.

Keywords: *CuO and TiO_2 Nanoparticles, Engine oil, Thermal conductivity, Viscosity.*

1. Introduction

Over the past years, there has been an on-going interest in the development and application of organic nanomaterials because of their unique properties such as semiconductors, catalysts, optical properties, anti-friction and magnetic [1]. The chemical engineering processes in the petroleum industry witness dramatic development due to nanotechnology applications. The production of lubricating oils regards an important process in the petroleum refineries to produce high-efficiency lubricants for many engines [2]. This process included a combination of many interacted fields such as chemistry, physics, and fluid mechanics. The main purposes of lubricating oils are to lubricate the moving parts, cleaning the system, prevent corrosion, improve performance, and cool the engine [3]. These lubricants must be qualifying the requirements of high lubricity with long lifetime for the internal combustion engines.

Lubricating oil gains properties by adding many chemical materials and principally Nano-additives. Hence, improving lubricating oils specifications is considered the main factor and important for saving total energy and conservation, that is given to the mechanical system [1, 3]. Additives enhance the ability of the lubricant relative to the parent oils by adding new properties or improving the desired specifications already presents [4]. For this reason, the modern formulated lubricants that enhanced by Nano-additives are the most integral part. On the other hand, the cost of final lubricating oil in the presence of additives still a dominant factor in determining the feasibility of such production processes [5, 6]. In recent years nanotechnology witnessed many applications in the petroleum and gas industry.

Nanofluids are one of the most important applications of nanotechnology in many fields of science and engineering rather than in petroleum refineries. Actually, when nanoparticles were added to any fluid a nanofluid is formed. Then, in the case of the lubricating oils, the addition of nanoparticles to base oil a nano-lubricants (nanofluid) is formed [7-10]. Many nanoparticles additives have been investigated to improve the tribological performance of the base lubricating oils for diesel engine applications. Most designers and authors have focused nanotribology in diesel engines with internal combustion, which can be considered as one of the most important key strategies for decreasing frictional power losses, combustion, saving fuel, reduction excessive heat generation and consumed fuel and cost of maintenance, exhaust emission, enhance heat transfer rate [11-16]. The types and specifications of nanoparticles such as: their nature, size, and physical and chemical properties are the key factors that determine the efficiency of nano-lubricants. On the other hand, the high surface area and high thermal conductivity of most nanoparticles make the nano-lubricants more stable with high performance than the base fluids for internal combustion engines [17, 18, 19].

Friction and wear of frictional surfaces, which can be reduced due to the incorporation of nanoparticle additives into the essential lubricant [20], the principal function of lubricating oils are to protect two metal surfaces wetted thus reducing friction, and avoiding wear [21]. It is also noted, that friction and scratches had a direct effected on the size, shape, type of material, and concentration of nanoparticles in base lubricating oils [22].

Wu et al. examine the effect of TiO_2, nano-diamond, and CuO nanoparticles on the tribological properties of different lubricants oil and observed that with CuO additive oils results of the properties are good corrosion control and friction reduction [23]. Thottackkad et al. had surveyed the effect of CuO nanoparticles as additives in the lubricating oils as (nano-fluids) [24]. Hwang et al. studied the effect of particle size and morphology of nanomaterials suspended in base oils on high performance of the lubrication [25]. Zhang et al. found in their investigated that Al_2O_3 nanoparticles additive used in base oils (lubricants) can be improved the friction reduction and antiwear that appear high performance of lubricating oils [26, 27]. The addition of titanium oxides NPs to the parent lubricants, these particles act on the formation of preservative films on the metal and thus shows constant friction on the surfaces [28]. Shenoy et al. [29] studied the effect of titanium oxides NPs additives in lubricating oils. Numerous of previous studies found out that the mixture of nanomaterials and lubricating oil reduced the friction coefficient and wear also increased the extreme pressure, which could make the bearing more durable [31, 32]. So when evaluating the properties of traditional lubricating oils it has been found them less efficient than the nano-lubricants, which produced from nanomaterials that have been added to the base oil. Then, the NPs become promising new lubricating oil materials which have important economic value on the friction-energy consumption. Zhang et al. [33], the overlapping layer between two surfaces will get better the smoothness of the prorated movement and prevented damage in a diversity of materials in many shapes such as: solid, liquid and gas. Choi et al. stated apparently that nanoparticles in lubricating oils can pad the scar and channels of the friction, and wear surfaces [34] as shown in Fig. 1.

It is important to mention here, that in the investigated present work focus on the enhanced the high-grade lubricating oil such as SAE 15W40 engine oil. Therefore, the main aim present work is to study the effect of adding CuO and TiO2 nanoparticles on the properties of diesel engine oils. Then, comparing between their properties such as viscosity, thermal conductivity coefficient, flash point, and also pour point of nano-lubricants.

2. Experimental Work

2.1 Materials

The SAE 15W40 engine oil and diesel fuel were attended from (Al-Dura Refinery, Middle Petroleum Company, Baghdad, Iraq). The SAE 15W40 lubricating oil is used as a parent fluid. Table 1 shows the specifications of used oil. NPs of CuO and TiO_2 are the best for many tribal engineering applications, especially in the field of lubricating oils because of their professional behaviour and superior properties. These NPs were selected for the present work. A calculated amount of CuO and TiO_2 NPs was buying from (Nanjing XFNANO Material Tech Co., Ltd). The CuO and TiO_2 10 nm and 25 nm were used mean diameter respectively. Tests tribological were conducted on heavy-duty multi-grade diesel engine oils (SAE 15W40). Table 2 shows main properties of CuO and TiO_2 NPs.

2.2 Measuring and Analyzing Apparatus

A bath ultrasonic (P120 Elmasonic, Germany) was used for homogenizing, dispersing and mixing of CuO and TiO_2 NPs and making so-called nanofluids. The thermal conductivity was measured by KD2-Pro (Decagon Devices, USA) of parent oil and nano-lubricant at different temperatures and concentration. Also, field emission scanning electron microscope (FESEM, Japan, JEOL 7610F), X-ray Diffractmeter (XRD, Japan, Shimadzu-6000), and Fourier transform infrared spectroscopy (FTIR-8400S, Shimadzu) was used for analysing the properties of copper oxide and titanium oxides.

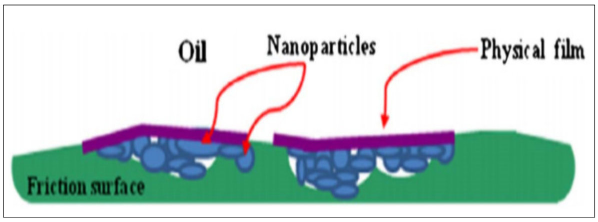

Fig. 1. Mechanism appearing how to reduce friction between oil surfaces when mixed with nanoparticles [34].

Table 1,
Properties of SAE 15W40 engine oil.

Property	Value
Viscosity at 100 °C (cSt)	14.5
Viscosity at 40 °C (cSt)	109.84
Viscosity index	135
Density at 15 °C (kg/m^3)	904
Pour Point (°C)	–27
Flash Point (°C)	220

Table 2,
The main properties of CuO and TiO_2 nanoparticles.

Specification	CuO	TiO_2
Color	black	white
Purity (%)	>99.9	>99.9
surface area (m^2/g)	263	220
Volume density (g/cm^3)	0.20-0.35	0.25
Density (g/cm^3)	6.4	3.9
Crystal form	sphere	sphere

2.3 Preparation of Nano-Lubricant

The nano-lubricants were prepared by addition of copper oxide and titanium oxides at different concentrations of 0.1 wt. %, 0.2 wt. %, 0.5 wt. %, and 1 wt. %, to parent lubricating oil (SAE 15W40). The required amount of CuO and TiO2 was carefully weighed using an accurate electronic balance and mixed with the parent oil. In the nanofluids preparation process, the (Two-step method) was used, due to more common, easier and more economical than the (One-step method) for production nanofluids.

Due to the high viscosity of the base fluid, the mixing process was achieved by using a mechanical mixer and bath ultrasonic (type, P120 Elmasonic, Germany) method is used for dispersing of NPs CuO and TiO_2 inside the parent fluid to obtain high desperation for nano-lubricants. The operating conditions values of the bath ultrasonic method can be recognized by power (100%), temperature (40°C), time (2-3 h), and frequency (20 kHz).

2.4 Rheological and Thermal Measurements of Nano-Lubricant

The thermal conductivity of nano-lubricants has been measured, for this purpose, KD2-pro, a laboratory and portable device, was used to analyse thermal properties. The device has a probe length of 60 mm and diameter of 1.3 mm, and the device measures the thermal conductivity based on hotwire technology. The parent oil and Nano-lubricants thermal conductivity that was measured at various concentrations and temperatures. The viscosity of parent oil and nano-lubricants with concentrations from 0.1 wt. % to 1 wt. % concentrations were measured at a temperature of 40 °C and 100 °C. Kinematic viscosity, flash and pour point of the parent oil and nano-lubricants were measured based on ASTM D-445, ASTM D-97, and ASTM D-92 respectively.

3. Results and Discussion

3.1 XRD Pattern and FE-SEM

The XRD pattern in the current investigation indicates the TiO_2 nanoparticles as shown in Fig. (2. a). It can be noticed that typical diffraction peaks are 2θ: 25.2°, 36.8°, 38.2°, 39.1°, 48.2°, 53.9°, 55.2°, 62.8°, 68.4°, 70.4° and 75.2° with sharp deviation peaks at 25.2° and 48.2°. More comparison between the JCPDS card No.

(JCPDS80 – 1268) with XRD patterns that the same file data also confirm, It can be seen, that the nanoparticles of TiO_2 are high-purity particles with single anatase structure phase. Additionally, from the XRD pattern in Fig. (3. a), it can be found that the CuO nanoparticles in the current investigation have the same major characterization peaks of pure copper oxide card No. (PDF Card - Cu O - 00-048-1548) at 2θ values of 32.2º, 35.4°, 38.6°, 48.5°, 52.9°, 58°, 61.3°, 65.5°, 67.8°, 72.3°, and 74.5°. Otherwise, in the XRD pattern, no other impurity peak was noticed, observing the formation of the single sample phase of CuO nanoparticles.

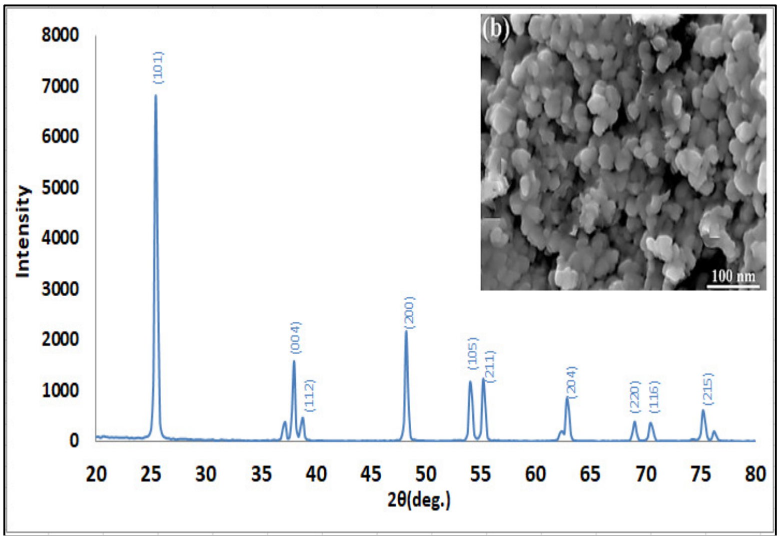

Fig. 2. XRD pattern (a) and FE-SEM (b) image of TiO_2 nanoparticles.

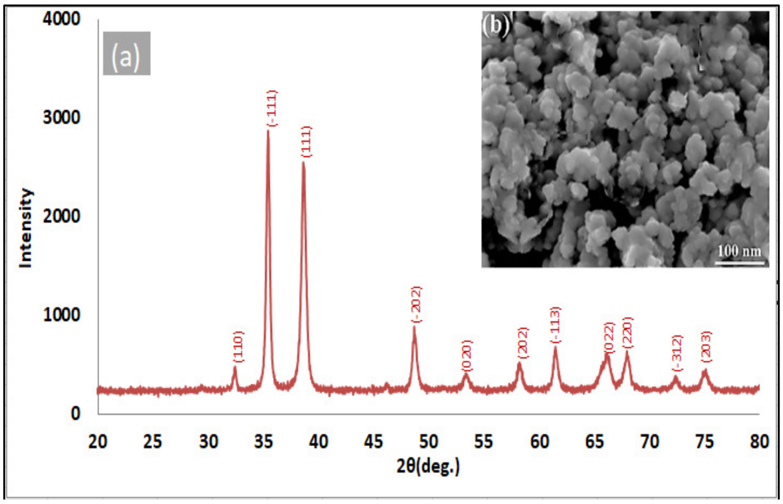

Fig. 3. XRD pattern (a) and FE-SEM (b) image of CuO nanoparticles.

The FE-SEM pictures in Fig. (2.b and 3.b) showed the morphology of the nanoparticles of CuO and TiO_2 respectively. The morphology of the titanium oxides and copper oxide nanoparticles were spherical to some extent, which is provided a good rolling mediator inside lubricating oil. The FE-SEM results show that the average particle size of CuO and TiO_2 is about 10 and 25 nm respectively. Also, it can be seen; majority nanoparticles are great agglomerates prior to dispersion as shown in the SEM image of CuO andTiO_2nanoparticles.

3.2 Properties of Prepared Nano-lubricants

In fact, the estimating of the suitable concentration is a well important issue to be realized best characteristics [12, 16]. For dispersing NPs CuO and TiO_2 inside the base oil, mechanical methods of bath ultrasonic and magnetic stirrer were used. In the present investigation, it was observed that samples by an ultrasonic process, the NPs were separated from each other, and not agglomerated. But samples which prepared by the bath ultrasonic method, the NPs are better distribution and more uniform dispersed compared with previous samples that prepared from other ways. All the samples inside were kept in transparent glass containers in a completely stagnant state for about 60 days to assess their own stability conditions as shown in Fig. 4.

During this interval, the stability is recorded of all the samples that checked visually periodically. On the other hand, it was observed that the dispersion of CuO and TiO_2 nano-additives within the base oil was very high through the period of checking; this gives an impression of the high stability of these materials within the lubricants, because of the high dispersion caused by the bath ultrasonic device.

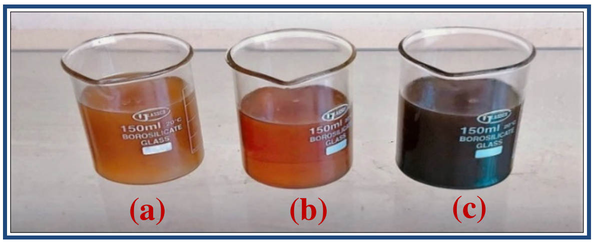

Fig. 4. The stability condition of nano lubricants after 60 days (a) TiO_2/oil (b) base oil, and (c) CuO NPs.

3.3 Viscosity

Fig. (5 and 6) show the viscosity amount in total has a rising tendency, with increased concentration of (CuO and TiO_2) NPs. When the higher the temperature of the oil, the viscosity decreased of all the samples significantly. And also it seems, by increasing the concentration of (CuO and TiO_2) NPs, for each 40°C and 100°C the viscosity increase.

The viscosity relative to the base lubricant increased by 2.42%, 7.1%, 10.88% for each concentration for copper oxide. And for titanium oxides the viscosity increased by 1.51%, 5%, 8.8%, which is linked to the nano-lubricant with concentration 0.2 wt.%, 0.5 wt.%, and 1 wt.% respectively and at 40 °C temperature, especially the concentration at 1 wt.% gave the highest ratio of viscosity improvement. The point interestingly with respect to the viscosity of nano-lubricants for in both additives nanomaterials with concentration 0.1% at both temperatures is that the amount of viscosity has a little reduction with respect to the base lubricants, but the viscosity gets it an upward direction with increased concentration of copper oxide and titanium oxides. Nanoparticles take an intermediate position between the oil layers when added, thus facilitating movement between the oil layers and sliding each other.

In the current work, the lubricating oils viscosity was decreased after inserted CuO and TiO_2 NPs at the level by 0.3%, 0.62% at temperature 40 °C and 100 °C respectively at 0.1 wt.% concentration with relative to copper oxide. While for the titanium oxides we did not notice any change in the viscosity at 0.1 wt. % concentration. On the other hand, we can conclude that the viscosity of the SAE 15W40 base lubricating oil did not undergo any significant changes when adding nanomaterials to a few concentrations. Therefore, the engine oil for the Considered is a function of the concentration of the added nanoparticles.

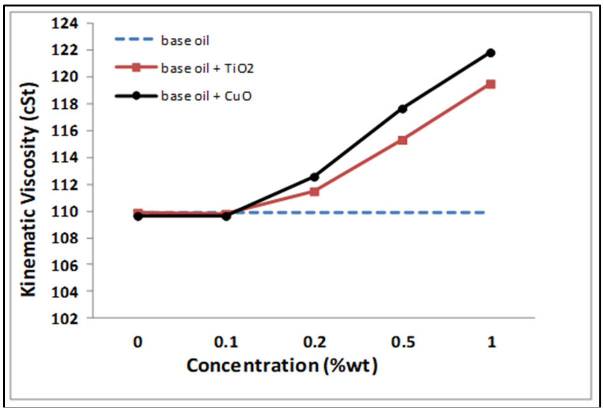

Fig. 5. The kinematic viscosity of nano-lubricants at 40 °C.

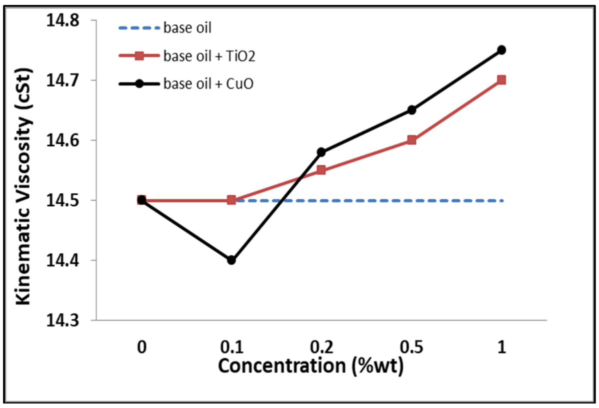

Fig. 6. The kinematic viscosity of nano-lubricants at 100 °C.

3.4 The Thermal Conductivity Measurement

Fig. (7 and 8) show the results for thermal conductivity determined of nano-lubricants after addition nanoparticles to parent oil and in different concentrations and also with different temperatures. It is also seen, that the results obtained from engine parent oil by the addition of nanoparticles CuO & TiO_2 at specific rates, was the thermal conductivity coefficient of the nano-lubricants much greater than the parent oil without additives.

On the other hand, can be high thermal conduction of nanoparticles such as CuO & TiO_2 one of the most important reasons for this phenomenon with attention to lubricating oil. Based on the results obtained, adding nanoparticles to SAE 15W40 engine parent oil, base on the method which has been done in this work, the amount of thermal conductivity at 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% concentrations of CuO & TiO2 had increased 9.85%, 15.2%, 19.73%, and 21.84% respectively with respect to CuO, while TiO_2 had increased 8.12%, 14.46 %, 17.93%, and 20.2% respectively. During this research, we reached a result where copper oxide has a high impact on the thermal conductivity coefficient of the engine oil compared to titanium oxides which have a positive effect of the major, but less than when the addition of copper oxide to lubricants.

As well, it can be observed that, when the temperature increased, the thermal conductivity of the nano-oil increased, this also applies to the concentration of nanoparticles, as the concentration increases, the quantity of thermal conductivity coefficient of the engine oil increased. However, it should be noted that, in the case of different type of basic fluids, the rate of concentration the nanoparticle, kind of nano-additives, the rate of dispersion of nanoparticles within the base fluid, and the method used for dispersion of nanoparticles inside the base fluid. The different parameters resulting from the previous reasons are the effect of the resulting changes in properties.

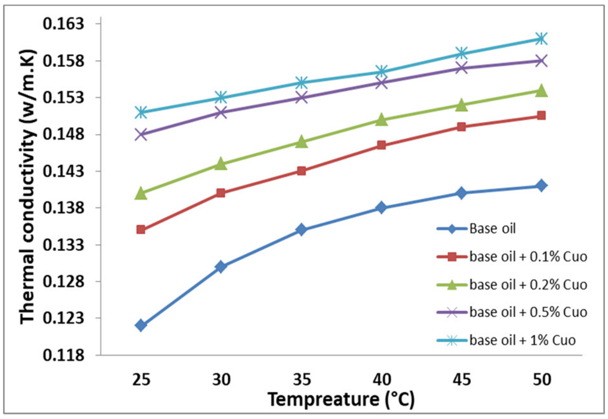

Fig. 7. Comparison of the thermal Conductivity between the parent oil and nano-lubricants at different temperatures and concentration.

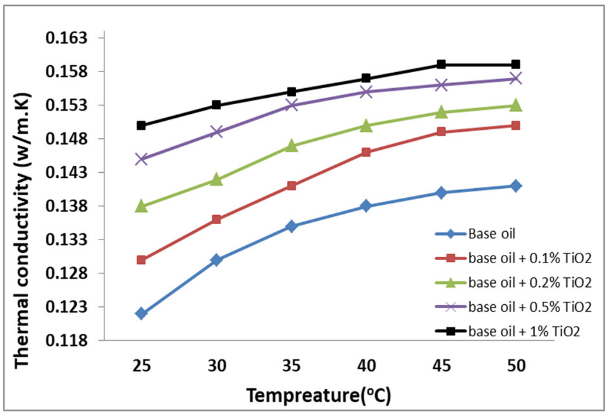

Fig. 8. Comparison of the thermal Conductivity between the parent oil and nano-lubricants at different temperatures and concentration.

Copper oxide and titanium oxides have greater potential than other nanoparticles to improving thermal conductivity coefficient of engine oils, due to the high thermal conductivity of these materials, especially the copper oxide. By taking a look at this property, that one of the functions of engine oil reducing the erosion of moving parts, removing some heat generated by friction and combustion between the parts to outside environment, so that helps to cool the engine. Oil works as a cleaner and removes dust and carbon particles between moving parts. Therefore, the using carbon nanotubes structures can be considered as a method to improve the thermal conductivity of diesel engine oils.

3.5 Flashpoint and Pour point

The flash point It can be said that is the minimum temperature where the vapour of lubricating oil is exposed to the air an ignition, burns in a moment and then turns off quickly. In this research, the direction of changes in the flash point is shown as a function of the concentration of NPs (CuO and TiO_2) in order to add it to engine oil in Fig. 9. It can be said that the flash point of oil is actually a determinant of the upper-temperature limits of the functions of that oil. It can be observed that the addition of NPs to the base oil has caused an effect and a change in the flashpoint which leads to its increase until it reaches a significant amount.

The flashpoint rate has reached an increased at additive nanoparticles in different concentrations 0.1 wt%, 0.2 wt%, 0.5 wt%, and 1 wt% of copper oxide and relative to the basic fluid is 7.27%, 10.9%, 14.1%, and 15.9% respectively, on the other hand, the titanium oxides nanoparticles give a perfect rate of increasing flash point at 4.54%, 9.45%, 11.81%, and 13.63% respectively. Although this relationship is not linear and it was noted that changes in weights at higher concentrations are less than changes in lower concentrations.

The pour point this property of lubricating oil is appraised as the marginal point of temperature, in which liquid cannot flow at this stage. The moment in which the engine starts working is the greatest rate of wear up to the engine machine. The lubricating oil does not reach all parts of the engine quickly when it is pumped, and to avoid and prevent such a problem and reduce its impact the lubricating oil must be sufficiently viscous stirred to flow easily and fast to reach all parts of the engine. The resulting changes in the rate of the parent oil point were studied under the effect of addition nanoparticles (CuO & TiO_2) at different concentrations as shown in Fig. 10.

Trends in changes in the pour point of oil as a function of the concentration of nanoparticles in oil lubrication with (CuO & TiO_2) nanoparticles with a concentration of 0.1% by weight, the spill point was reduced slightly, and at a 0.2% concentration at 6.9%, there was raised in the pour point. Yet, when the concentration of nanoparticles increased to 0.5% by weight and 1% by weight, the pour point was reduced again.

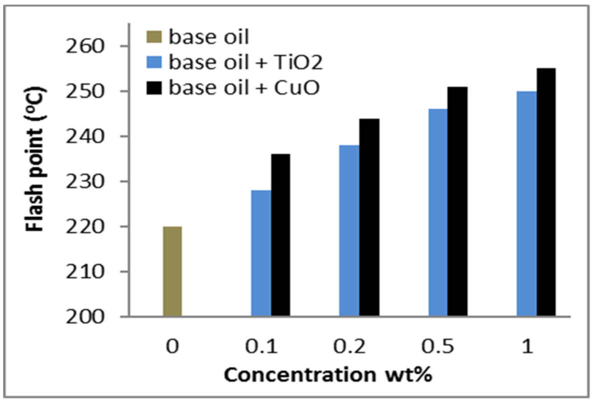

Fig. 9. The flash point values of parent oil and nano-lubricant.

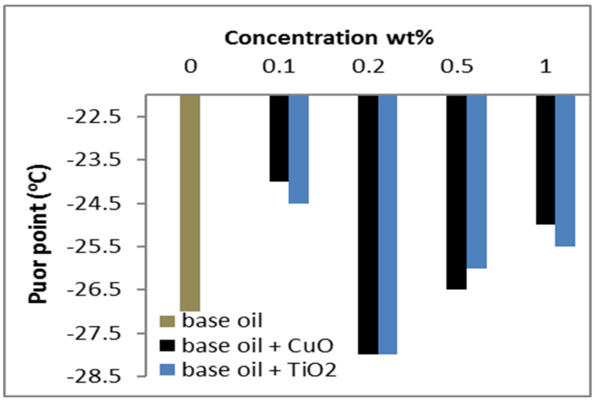

Fig. 10. The pour point values of parent oil and nano-lubricant.

It can be concluded, that increasing thermal conductivity coefficient by adding copper oxide and titanium oxides nanoparticles is due to increased oil resistance against ignition, It can be seen, by estimate the produced change in the rate of pour point and flash point of nano-oil after adding nanoparticles, which were dependence as a function of concentration, the best amount noticed of both parameters have 0.2% by weight concentration.

4. Conclusions

It was concluded that the dispersing of NPs in lubricating oil to form the nano-lubricant is a very complicated process in high viscosity oil. It was observed that CuO and TiO_2 have been distributed in different concentrations by using the bath ultrasonic method within the lubricating oil to obtain the best stability, due to they provide high energy and prevent their aggregation and precipitation again.

The results observed that thermal conductivity and flash point by the effected addition NPs may change for the better at a high rate, but the oil properties such as viscosity and pour point have no perceivable concrete changes in the least nanoparticles concentration 0.1% by weight. The thermal conductivity increased CuO/oil and TiO_2/oil about 12.62% and 9.3% respectively at 0.1 % wt. concentration. Also, a flashpoint for both nano-lubricants prepared increased by about 7.27% and 4.45% respectively.

Conclude that the nano-lubricant prepared with 0.2 wt. % concentration of CuO/oil & TiO_2/oil, it seems that is the better sample for both because in this sample viscosity had unchanged much, this is desirable, thermal conductivity and other oil specifications have been improved. On the other hand, a comparison that observed results from assay the effects of CuO and TiO_2 on the characterizations of engine oil appear that, CuO NPs have a better functionality for improving the characteristics of SAE15W40 engine oil than TiO_2 NPs.

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الخصائص الريولوجية والحرارية لزيوت التزييت المحسنة بوسطاة تأثير المضافات النانوية أوكسيد النحاس و أكاسيد التيتانيوم

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الخلاصة

مواصفات زيت التشحيم هي في الأساس نتيجة لإضافة مادة تستخدم لإنتاج الخصائص المرغوبة أو تحسينها. في هذا البحث ، تمت إضافة أكسيد النحاس (CuO) وأكسيد التيتانيوم (TiO_2) النانوية الكروية إلى زيت محرك SAE (15W40) لدراسة الموصلية الحرارية، والاستقرار، ولزوجة مواد التشحيم (النانوية ، والتي تم إعدادها بتركيزات مختلفة من (٠,١٪ ، ٠,٢٪ ٠,٥٪ ، ١٪) بالوزن ، وأيضاً نقطة لأنسكاب ، ونقطة الوميض بوصفها معلمات جودة خمسة. تظهر النتائج التي تم الحصول عليها، أن الجسيمات النانوية (CuO) في جميع الحالات ، تعطي أفضل وظيفة وتأثير على زيت المحرك فيما يتعلق (TiO_2). عند التركيز ٠,١٪ بالوزن، ارتفعت الموصلية الحرارية من (oil / CuO) و (oil/ TiO_2) بنسبة (٧,٢٧ ٪ و ٤,٥٤ ٪) على التوالي. في الوقت نفسه ، ارتفعت نقطة الوميض بنسبة (١٢,٦٢٪ و ٩,٣٪) على التوالي مقارنة مع زيوت التشحيم الأساس.