Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

8th International Conferenc
on
Chemical & Environmenta
Engineering
19 – 21 April 2016

TANM -2

Re-evaluation of the properties of a selected lubricant after adding Zinc oxide as a Nanoadditive

S. M. El Abed[1], E.A. El –Sherbini[2], M. B. Mohamed[3]

Abstract

This study includes synthesis of ZnO nanoparticles in organic media using Oleylamine and Oleic acid. Then survey the effect of ZnO nanoparticles on the properties of lubricant oil, The result show that, addition of ZnO nanoparticles with concentration of 0.05 (wt%) improve flash point by 3% also reduce scar diameter by 3.12 % with respect to pure lubricant, While there are no effect on pour point, thermal stability and viscosity of pure lubricant. The investigation of morphology and structures of nanoparticles carried out by TEM, XRD, FT-IR.

Keywords: Nanoparticles, Lubricant, Flash point, Wear, Viscosity

----

[1]Chemistry administration, Ministry of Trade & Industry, Cairo, Egypt, Shima321321@gmail.com

[2] Prof. Of laser application in Metrology, Photochemistry and Photobiology and Agricultural, National Institute of Laser Enhanced Sciences, Cairo University, Egypt

[3] Lecturer of chemistry at National Institute of Laser Enhanced Sciences, Cairo University, Egypt

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

I.C.E.E.2016

8th International Conferenc
on
Chemical & Environmenta
Engineering
19 – 21 April 2016

l. Introduction

Nanoscopic materials and nanoparticles have a great attention in recently due to special properties which cannot provide by bulk materials, they have several application in many field such as catalysts (1), solar cell (2), optoelectronic and imaging (3), thin film coating (4,5) and also used in lubricant as an additives to improve its properties.

Many papers reported use nanoparticles as lubricant additives to improve tribological properties of lubricants rather than pure lubricant. S. Bhaumik and S.D. Pathak (6) investigated the wear reduction of CuO nanoparticles additives in mineral oil using pin on disk apparatus and they observed that (0.2 wt %) of CuO nanoparticles decrease coefficient of fraction (28.5% approx.) and reduce rate of wear (70% approx.) as compared with pure mineral oil also flash – fire points, viscosity, viscosity index increase with increase nanoparticles concentration.

Jun Zhao et al (7), study the tribological characteristics of a multilayer grapheme and nanosheets MoS_2 as aviation hydraulic oil additives under temperature range 25-125 °C and observed that in case of MoS_2 a high temperature lead to higher friction coefficient, on the contrary in case of multilayer graphene the fraction coefficient becomes a little higher and more unstable with increase temperature over 75°C. Also they observed in present of MoS_2 the specific wear volume loss is much smaller than that of multilayer grapheme case. Christina et al (8), reported pyrazole –pyridine silver complex is evaluated as friction reducing agent and antiwear additives in engine oil at temperature which thermally degrade the base oil, Teresa Díaz-Faes López et al, (9)sed grafting hydrophobic SiO_2 nanoparticles as a lubricant additives and they found these nanoparticles reduce drastically the waste of energy in fraction process and more environmentally friendly than other additives. Monica Ratoi et al, (10) study the mechanism of using WS_2 as lubricant additives in high pressure contacts and they observed an uniform tribofilm was generated lead to reduce both fraction and wear in high pressure sliding contacts. Yue Gu et al, (11) re-evaluate of tribological properties in present of dual coated TiO_2 nanoparticles and the result show that dual coated TiO_2 nanoparticles improve the load carrying capacity, the fraction reduction also wear scar diameter and coefficient of fraction of water base lubricant fluid decrease with increase TiO_2 nanoparticles concentration, this due to the formation of adynamic deposition film during rubbing process. Many study used ZnO nanoparticles as a lubricant additives to improved tribological properties of lubricants (12, 16)

In this study, we survey the effect of ZnO nanoparticles on the lubricant oil properties such as viscosity, flash point, pour point, thermal stability, antiwear and compare the results with the pure lubricant results.

2. Experimental

2.1. Chemical materials

Pure lubricant oil from Miser of Petroleum Company, Zinc acetate dihdrate, and Oleic acid from Oxyford, Oleylamine from Sigma and were used without more purification.

2.2. Synthesis of ZnO nanoparticles

5 g of Zinc acetate dehydrate dissolved in 120 ml of oleylamine, heated to 200°C with continues stirring then add 30 ml oleic acid and leave it 2 h with stirring. Filtrate the precipitate and dried at 60 °C. To prepare a nanolubricant, different concentration (0.05, 0.1, 0.2 wt %) of ZnO nanoparticles dispersed in pure lubricant oil using an 40 Hz ultrasonic probe for 10 min.

Table (1) Specification of pure lubricant and the accuracy measurement of ASTM standards

Spacification	Value	ASTM standard	accuracy
Viscosity at 40°c	49.4 cent stock	ASTM D 445	0.26%
Viscosity at 100°c	7.13 cent stock	ASTM D 445	0.26%
Flash point	230 °c	ASTM D 92	± 8 °c
Pour point	-2 °c	ASTM D 97	± 3°c

2.4. Instrumental analysis:-

- The morphology of ZnO nanoparticles and their size investigated with JEOL JEM-2100 transmission electron microscopy at an accelerating voltage of 200 kv, and powder X- ray diffractometer used to identify the phase of ZnO nanoparticles.
- Infra Red spectra of ZnO nanoparticles was obtain using KBr disc in the wavelength rang of 4000- 500 cm^{-1} with Thermo scientific nicolet IS50 FT-IR spectrometer.
- Kohler apparatus model K23700 with accuracy ± 0.02°C used to measure viscosity of pure lubricant and lubricant with three different concentrations of ZnO nanoparticles at 40°Cand 100°C, according to ASTM D 445.
- Semiautomatic Cleveland open flash apparatus used to measure flash point for both pure lubricant and nanolubricant according to ASTM D 92.
- Seta Cloud-and Pour point refrigerator model 93531-7 with temperature range from ambient to -51°C used to measure pour point of both pure lubricant and nanolubricant According to ASTM D 97.
- Rotary vessel test apparatus with copper catalyst coil at 150°C, 6.2 bar and 100 rpm at an angel of 30° from the horizontal, used to measure thermal stability of pure lubricant and nanolubricant with 0.05 wt% ZnO nanoparticles, according to ASTM D 2272.
- Antiwear ability of both pure lubricant and nanolubricant with 0.05 wt% ZnO nanoparticles measured using four ball machine, with 40 Kgf at 75°C and 1200 rpm for 60 min. according to ASTM D 4172.

3. Results and discussion

3.1. Deposition of CNT from coconut oil on different substrate

3.1.1. TEM images:

The shape and size of the nanoparticles were determined by Transmission Electron Microscopy (TEM), with a JOEL- JEM -2100 microscope operating at an accelerating voltage of 200 kV. A drop from a very dilute sample solution was deposited on an amorphous carbon-copper grid and left to evaporate at room temperature. The size and shape of the sample as illustrated in Fig.(1) shows that the average particle sizes is about 40 nm ± 10 nm and the particle shape is spherical.

3.1.2. XRD patterns:

X-ray pattern of the nanoparticles was performed on an X-ray diffractometer using Cu (Kα) radiation, The wavelength used for the XRD analysis is 1·50546 Å and the running conditions for the X-Ray tube are 40 kV and 40 mA with 2θ ranged from 10°- 90°. Fig. (2) shows diffraction peaks at (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes that are in good match with the common ZnO hexagonal wurtizite structure of ZnO (JCPDS card No. 36–1451, with cell parameters a = b= 3.2501 Å, c = 5.2071 Å, space group: P63mc (1 8 6)) and confirm that the prepared ZnO is well crystallized. Table (2) illustrate the particle size estimated by Scherrer's equation ($D= K \lambda / \beta \cos \theta$, Where λ is the X-ray wavelength, β is the full wavelength of half maximum (FWHM) which measured using Gaussian curve of the Peak, θ is the half diffraction angle, and K is the shape constant taken as 0.9), where the average crystallite size of the particles are about 43.9 nm which agree with the result obtain from TEM, The small size and the hexagonal structure of zinc oxide nanoparticles play an important role in lubrication processes by filling microcracks of friction surfaces (17).

Table (2) the crystallite size of the particles estimated from FWHM

Position (2θ)	d value (A°)	Intensity (count)	Area	FWHM	Crystal Size L (nm)
31.66186	2.82127	45.4	19.31672	0.28862	48.7
34.32635	2.60835	28.5	15.14362	0.36583	39.2
36.14409	2.4814	73.6	34.39567	0.32020	43.9
47.43381	1.91411	20.4	8.72534	0.32460	45.6
56.4727	1.62709	31.6	14.2622	0.34328	44.8
62.7499	1.47882	28.2	16.6762	0.33075	47.9
66.22719	1.40859	4.1	1.9847	0.36825	43.9
67.8515	1.37925	20.7	13.4684	0.34597	47.2
68.96546	1.36019	11.2	4.8368	0.44448	36.9

3.1.3. FT-IR Spectra:-

The FTIR is a very useful tool to confirm formation of ZnO crystal and protect any adsorbed species on its surface. Fig. (3) shows peak at 434 cm^{-1} which is characteristic stretching mode of ZnO crystal, also peaks at 1604 cm^{-1} and 578 cm^{-1} are devoted to stretching vibration of COO-Zn and deformation vibration of Zn-O, respectively. Peaks at 1700 cm^{-1}, 1377 cm^{-1} are corresponding to symmetric and asymmetric stretching vibration of free C=O group of oleic acid, respectively. Peak at 722 cm^{-1}related to C-O bending vibration. Peaks at 2922 $cm^{-1,}$ 2726 cm^{-1} are representing C-H stretching mode of oleylamine carbon chain and peak at 3400 cm^{-1} for O-H stretching mode. Number of peaks between 800 cm^{-1} – 1400 cm^{-1} are devoted to asymmetric stretching of CH_2 group, terminal CH_3 group and =CH group of oleylamine. From observations we suggest that oleylamine and oleic acid form a monomolecular layer on the surface of ZnO nanoparticles and act as capping ligands to control growth of nanoparticles.

3.2. Measuring of viscosity

Viscosity define as resistance of oil to flow, It response on the efficiency of protective film between two working surfaces when they are pressed hard together under heavy loading, The oil film may be squeezed if he film has sufficient strength and thickness and will stay but if not it will rupture and metallic surfaces will make contact and scuff. So by measuring the viscosity of nanolubricant contain (0.05, 0.1, 0.2 wt %) of ZnO nanoparticles and compare the result with the viscosity of pure lubricant at 40°c and 100°c fig. (1a,1b), show that viscosity has a direct relation with nanoparticles concentration, and the highest increase related to the nanolubricant contain 0.2 wt% ZnO nanoparticles is 4.4% with respect to the pure lubricant at 40°C, while in nanolubricant contain the lowest nanoparticles concentration has slightly decrease rather than pure lubricant, That is because nanoparticles interputed between oil layer make it easy move on each other which lead to slightly decrease while by increase nanoparticles concentration, they agglomerated and prevent oil layer to move on each other and the viscosity increase.

3.3. Measuring of flash point and pour point:-

Flash point is the lowest temperature at which auto-ignition of the vapor occure above
The heated oil sample and it defines the degree of safety in using oil. The result of measuring flash point of pure lubricant and lubricant contain 0.05, 0.1, 0.2 wt% of ZnO nanoparticles in fig. (5) show that the addition of nanoparticles to the pure lubricant increases the flash point and there is a direct relation between flash point and concentration of nanoparticles, although the rate of increase of flash point in lower nanoparticles concentration is greater than the rate of increase in higher nanoparticles concentration.
Pour point is the temperature at which oil ceases to flow, it is a measuring the lowest temperature at which the oil flow by gravity alone, the effect of different concentration of

nanoparticles on pour point with respect to pure lubricant is recorded in fig. (6). and we noted that there is no increase in pour point due to addition of nanoparticles to pure lubricant.
Pour point is the temperature at which oil ceases to flow, it is a measuring the lowest temperature at which the oil flow by gravity alone, the effect of different concentration of nanoparticles on pour point with respect to pure lubricant is recorded in fig. (6). and we noted that there is no increase in pour point due to addition of nanoparticles to pure lubricant.

3.4. Measuring thermal stability:-

Degradation of lubricant oils by oxidation lead to a dramatic loss of its performance in service by formation of acids or sludges and resins, increase viscosity and loss of electrical resistivity. So by examine uses of ZnO nanoparticles as antioxidant and while the lowest nanoparticles concentration has not applicable change in viscosity with respect to the pure lubricant, It was chosen to measure thermal stability. The result in fig. (7) shows that no increase in thermal stability by adding ZnO nanoparticles.

3.5. Measuring antiwear ability:-

Antiwear ability of nanolubricant determined by measuring scar diameter reduction of lubricant contain ZnO nanoparticles rather than lubricant without nanoparticles . Fig. (8) shows that lubricant contain 0.05 wt% surface ZnO nanoparticles has scar diameter less than lubricant alone by 3.12 % which result to penetration of nanoparticles to the contact area and formation of protective film.

4. Conclusion

Preparation of nanoparticles in organic media provides a suitable dispersion of nanoparticles inside lubricant oil and prevents their agglomeration. With three concentrations of ZnO nanoparticles, Viscosity and flash point have a direct relation with nanoparticles concentration. Lubricant with 0.05 wt% of ZnO nanoparticles has not applicable change in viscosity and has notable improvement in Flash point and antiwear ability by rates 3%, 3.12%, respectively. While no improvement in pour point and thermal stability rather than pure lubricant oil.

5. References

[1] T.C. Charles, C. S. James, Y. X. Yao, E. M. Karp and T. L. Silbaugh, Insights into catalysis by gold nanoparticles and their support effects through surface science studies of model catalysts, The Royal Society of Chemistry 152 (2011) 227–239.
[2] C. Er-Chieh Cho, H. Jui-Hsiung , L.Chiu-Ping , J. Cai-Wan Chang, L. Kuen-Chan, H. Jen-Hsien, The optoelectronic properties and applications of solution-processable titanium oxide nanoparticles, Organic Electronics 18 (2015) 126–134.

[3] L. Zhu, J. Qin, and C. Yang, Synthesis, photophysical properties, and self-assembly behavior of amphiphilic polyfluorene: unique dual fluorescence and its application as a fluorescent probe for the mercury ion, J. Phys. Chem. B, 114 (2010), 14884–14889.

[4] R. Tânia, B. Carlos, P. José, S. Farinha, Functional Films from Silica/Polymer Nanoparticles, Materials 7, (2014), 3881-3900.

[5] D. T. Jessica, L.K. Teresa, F.G. Lauren, Processing and Characterization of Nanoparticle Coatings for Quartz Crystal Microbalance Measurements, Journal of Research of the National Institute of Standards and Technology. 120 (2015).

[6] S. Bhaumik, S.D. Pathak, Analysis of Anti-Wear Properties of CuO Nanoparticles as Friction Modifiers in Mineral Oil (460cSt Viscosity) Using Pin-On-Disk Tribometer, Tribology in Industry, 37 (2015) 196-203.

[7] Z. Jun, W. Yongfu, W. Wei, H. Yongyong, L. Jianbin, C. BeiJing, T. Hisakado, T. Tsukizoe, H. Yoshikawa, An Investigation on Tribological Properties of Graphene and MoS2 Nanoparticles as Additives in Aviation Hydraulic Oil, Stel dallas (2015) 17-21

[8] P. T. Christina, B.Irene , S. Matthew, D. Massimiliano, B. Hassan, W.C. Yip, M. Luciano, J.M. Tobin, Q. Jane Wang, Silver-Organic Oil Additive for High-Temperature Applications, Tribol Lett 52 (2013), 261–269.

[9] D.L.Teresa, F.G. Alfonso, D.R. Ángel, M. María,E.G. Marta, B.L. Rosana, Engineered silica nanoparticles as additives in lubricant oils, Sci. Technol. Adv. Mater. 16 (2015) 11pp.

[10] R. Monica, B.N. Vlad, W. John, Z. Jurgita, Mechanism of Action of WS2 Lubricant Nanoadditives in High-Pressure Contacts, Tribol Lett DOI 10.1007/s11249-013-0195-x, (2013).

[11] G.Yue, Z. Xiuchen, L.Ying, L.Yunxia, Preparation and Tribological Properties of Dual-Coated TiO2 Nanoparticles as Water-Based Lubricant Additives, Journal of Nanomaterials (2014).

[12] H.R. Ghaffarian, M. Saiedi, M.A.Sayyadnejad, Synthesis of ZnO Nanoparticles by Spray Pyrolysis Method, Iran. J. Chem. Chem. Eng, 30, (2011), 1.

[13] F.T.Marinalva, I.F. Edja, S.B.Kandice, M.A. Salete, Study of Oxide Nanoparticles as Additives for Vegetable Lubricants, Materials Research, 17(2014) 1124-1128. M.G.Veerendra, K. Anil Kumar, Synthesis, Characterization and Anti-Wear

[14] Properties of CuO-ZnO Nano lubricant, International Journal of Innovative Research in Science, Engineering and Technology, 3 (2014).

[15] Kalyani1, V. Jaiswal, R. B. Rastogi, D. Kumar, The investigation of different particle size magnesium-doped zinc oxide (Zn0.92Mg0.08O) nanoparticles on the lubrication behaviour of paraffin oil, Appl Nanosci, 2015.

[16] J. Qian Jianhua, Y. Zhang, L. Wang Lingling, J. Xing, Study on Lubrication Properties of Modified Nano ZnO in Base Oil, China Petroleum Processing and Petrochemical Technology,13 (2011) 69-73.

[17] V. An, Y. Irtegov, E. Anisimov, V. Druzyanova, N. Burtsev, M. Khaskelberg, Tribological properties of nanolamellar tungsten disulfide doped with zinc oxide nanoparticles, Springerplus, 4 (2015) 673.

Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

I.C.E.E.2016

8th International Conference on Chemical & Environmental Engineering
19 – 21 April 2016

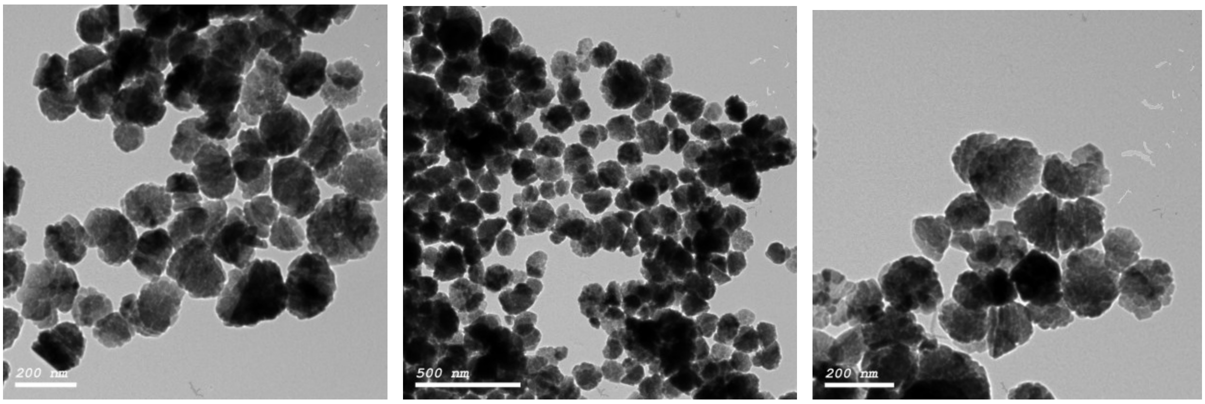

Fig. (1) TEM images of ZnO nanoparticles

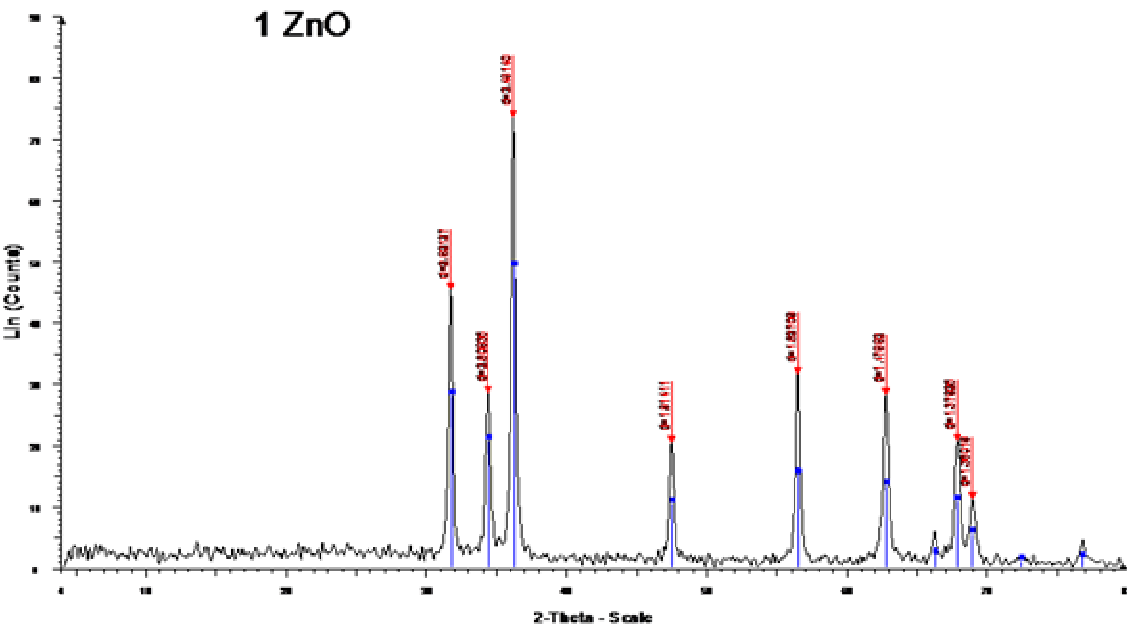

Fig. (2) X-ray diffraction pattern of ZnO nanoparticles

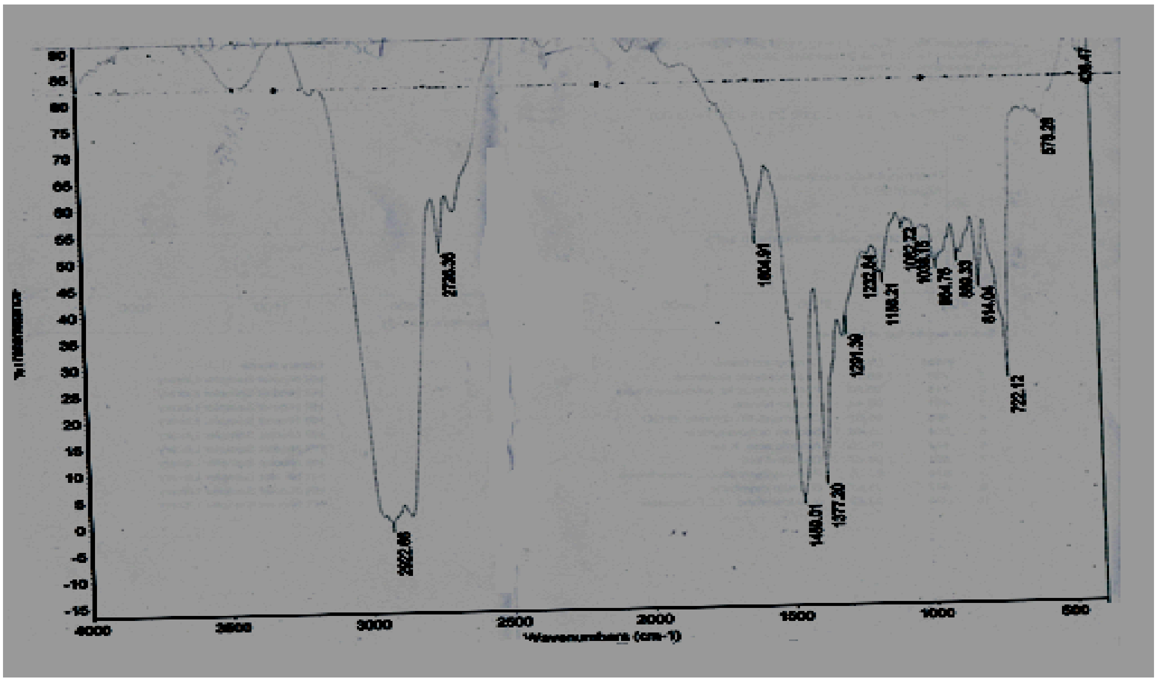

Fig.(3) FTIR of ZnO nanoparticles prepared in oleylamine and oleic acid

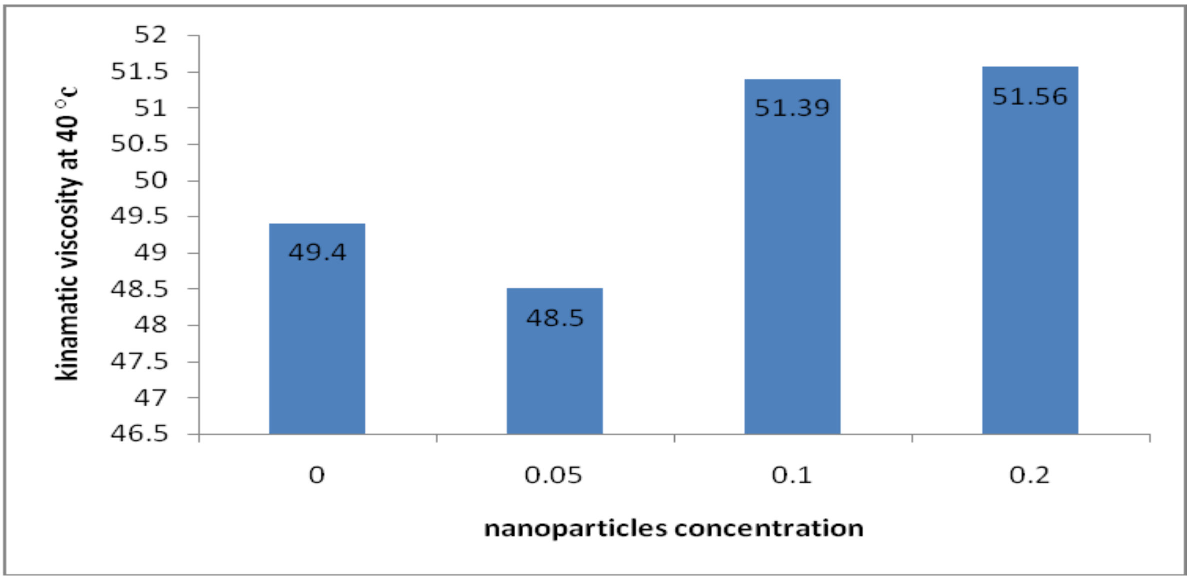

Fig. (4a) kinematic viscosity at 40°C of base oil and different concentration of nanoparticles

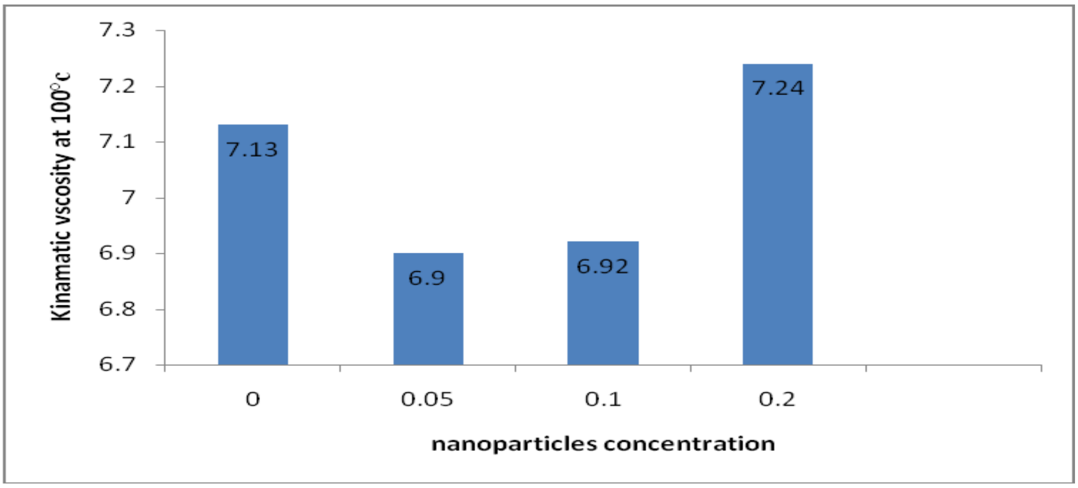

Fig. (4b) kinematic viscosity at 100°C of base oil and different concentration of nanoparticles

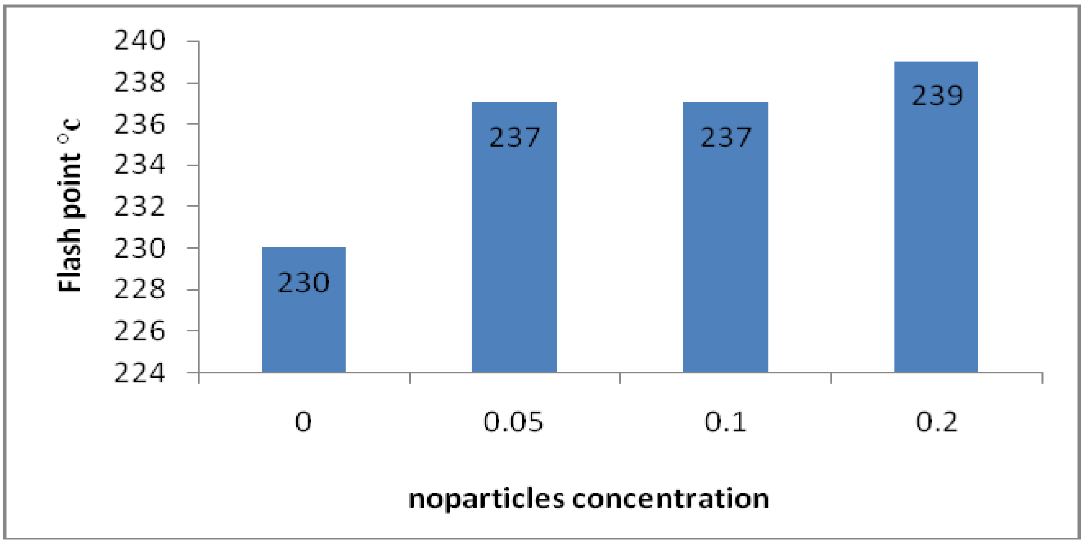

Fig. (5) Flash point of base oil and different concentration of nanoparticles

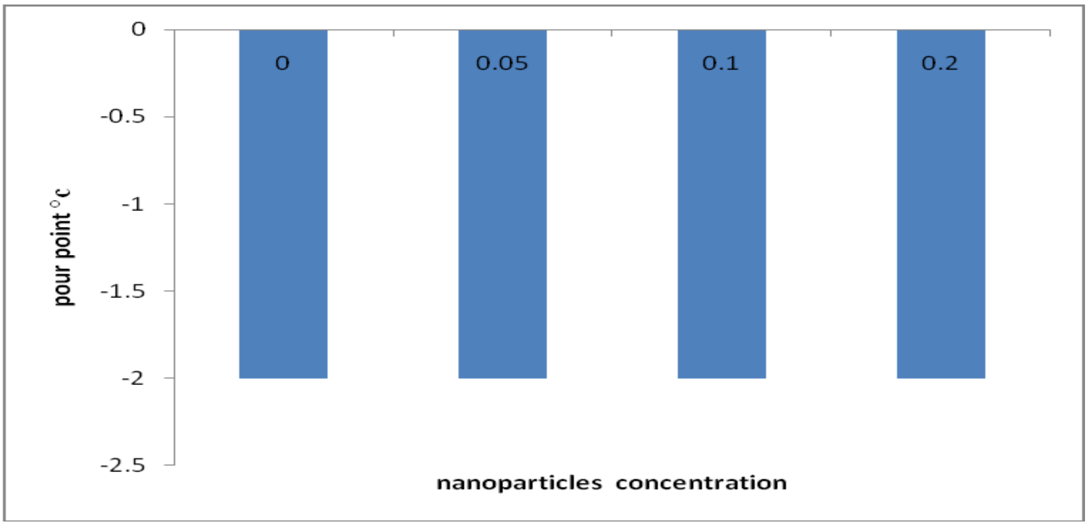

Fig. (6) Pour point of base oil and different concentration of nanoparticles

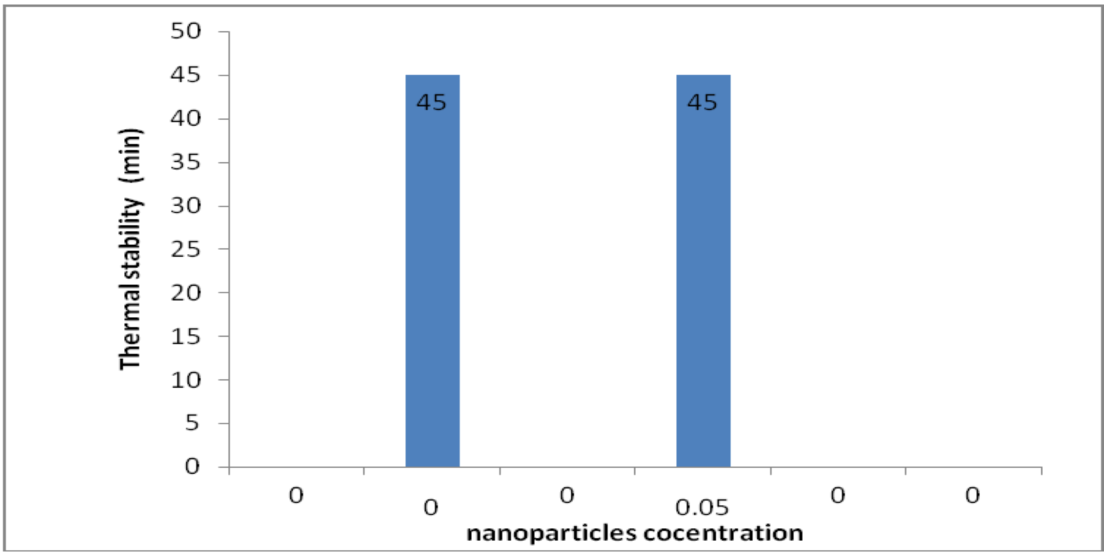

Fig. (7) Thermal stability of base oil and 0.5 wt % of nanolubricant

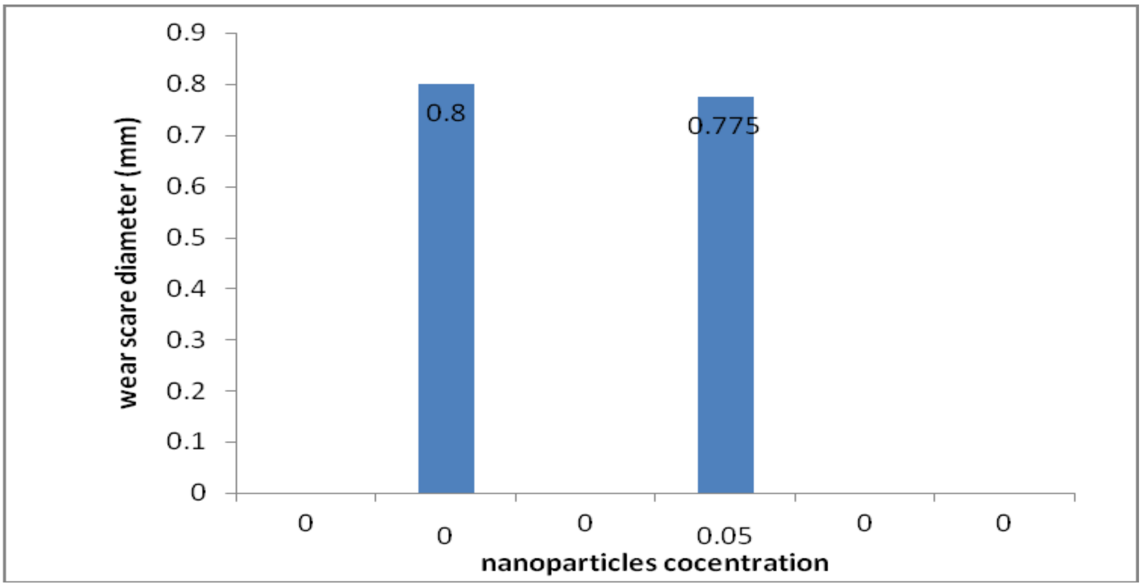

Fig. (8) Wear scare diameter of base oil and 0.5 wt % of nanolubricant