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Preparation of CuO Nanoparticles for Improving Base Oil Properties

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Abstract

Through this research, copper oxide nanoparticles were prepared via precipitation method using copper nitrate as a starting material. The resulting nanomaterial characteristics were diagnosed using available technologies such as AFM, XRD, B.E.T. surface area, pore-volume, pore size, and FTIR.

For modern industries, lubricants are efficient materials for reducing friction between moving surfaces. CuO nanoparticles are used as an additive that is dispersed in an oil phase. Ultrasound technique was used to disperse the nanomaterial in Stocks 60 base oil, and the effect of the ratios of the added nanomaterial on the final properties of the oil was studied. A ratio of 0.5, 1, 1.5, and 2% was used and mixed with an approbate amount of oleic acid and was dispersed using ultrasound.

The prepared copper oxide nanoparticles had an average particle size of 31.76nm and crystallinity of 93.63%. The surface area was around 27.61 m^2 / g. Diagnostic tests were carried out on the oil, as it led to an increase in the viscosity index gave high stability and good dispersion of the nanomaterial for a long time, as the viscosity index was re-examined during successive periods. The final characterization of the oil shows a good improvement in the viscosity index of 110 and the flashpoint increased to 240 ° C. By increasing the viscosity index leading to ease movement inside the tools and contact surfaces oil will overcome the severe conditions during operations.

Keywords: Nano additives materials, Lubricating oils, copper oxide nanoparticles, Base oil.

1. Introduction

Copper oxide nanoparticles are used in many applications such as additives to oils, gas sensors, photodetectors, etc. copper oxide nanostructures have various morphology

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including nanoparticles, nanosheets, nanowires. There are many methods used to prepare copper oxides such as hydrothermal, chemical precipitation, and microwave irradiation.

Lubricating oils can be produced by modern methods of refining from most crude oils. They may be distillates or residues derived from the vacuum distillation of a primary distillate with a boiling range (300-600 ºC). They range from thin, easily flowing spindle oils to thick cylinder oils. The uses of lubricating oils are legion, and it would be impossible to make directly from the crude oil all the various grades required. A limited number of primary oils are therefore manufactured at the refinery and these are blended in various proportions with or without additives to produce oils with the required properties.[1]

The most important property of lubricating oil is its viscosity, which is a measure of its internal friction or ability to flow, and largely determines its suitability for any particular application.

The viscosity of oil decreases with a temperature rise but to a varying degree depending on the type of crude oil from which it is derived and the refining treatment to which it has been subjected. The relationship between viscosity and temperature is of significance for lubricating oils since most oils have to operate over a range of temperatures. There are many ways of expressing this relationship but the one firmly established in the petroleum industry is the viscosity index (VI) system, even though it is an arbitrary system and more fundamental methods have been suggested.[2]

Engine lubricating oil must perform several functions [3]. It should:

- Reduce friction and wear between moving surfaces.
- Remove heat caused by friction.
- Provide a seal against escaping gases.
- Keep the engine clean by holding carbon and slug-forming material in suspension, so they will be removed by the oil filter or when the oil is changed.
- Provide protection against rusting and attacks by acids.

Auxiliary materials are added to lubricating oil to enhance their properties in one direction or another to meet the requirements of special applications, which are commonly employed. Known as additives are the more important of the numerous materials that have been proposed for this purpose [4].

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Each added substance is chosen for its capacity to perform one or more particular capacities in combination with other added substances. Chosen added substances are defined into bundles for utilization with a particular oil base stock and an indicated end-use application. The biggest conclusion utilize is in car motor crankcase greases. Other car applications incorporate pressure-driven liquids and adapt oils. In expansion, numerous mechanical oils and metalworking oils moreover contain LOAs. The major useful added substances sorts are dispersant, cleansers, oxidation inhibitors, anti-wear specialists, extraordinary pressure (EP) added substances, and viscosity index (VI) improvers.

Nano prepared copper oxide(CuO) using a sol-gel method using copper chloride($CuCl_2$), acetic acid(CH_3COOH), and sodium hydroxide (NaOH) at a temperature of 100oC. The final product has a size of 53nm. [5] and [6] Copper oxide was synthesized by chemical precipitating methods using two precursors copper nitrate (Cu(NO3)2.3H2O) and copper chloride(CuCL2). The results showed that the calcination process can effectively remove all the impurities and get better crystallization of CuO also different precursors used has a strong influence on shape, size, and morphology for CuO nanostructure. [7].

Copper oxide nanoparticles were synthesized by the chemical liquid deposition method using copper nitrate, ethyl acetate, and sodium hydroxide. Results showed that the final size of prepared CuO was between 50-70 nm. [8],[9]

2. Physical properties of Lubricating oil

The properties considered important are: -

- Viscosity.
- Viscosity change with temperature (VI).
- Pour point.
- Oxidation resistance.
- Flashpoint.
- Boiling temperature.
- Acidity (neutralization number)[10].

2.1.1 Viscosity

The viscosity of a fluid can be described as its internal friction, i.e. the resistance it offers to

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movement, either to a foreign body through it or from it against a foreign body. It can be measured by timing the flow of a given volume of fluid through a tube properly calibrated by the capillary volume. The result is kinematic viscosity, expressed in cent stocks. If this value is multiplied by the density of the liquid, the answer appears in absolute viscosity percentiles >1. Viscosity depends on temperature and decreases with increasing temperature; So the temperature should always be specified when starting the viscosity of the material. [1].

2.1.2 Viscosity Index

The rate of altering viscosity with temperature is communicated by the viscosity index (VI) of the oil. The higher the VI, the littler its alter inconsistency for a given temperature alter. The VI values for common oils extend from negative values for oils of naphthenic minerals to around 100 for paraffinic metals. Uncommonly prepared oils and chemical added substances can contain 130 and over [1].

Additives used as VI improvers include oil-soluble olefin copolymers with an average molecular weight in the region of 20,000, fatty alcohol methacrylate/lower alcohol ester copolymers in the range of 20,000 to 250,000, alkyl styrene copolymers in the region of 50,000 and vinyl acetate/fumarate fatty alcohol ester copolymers in the region of the area of 100,000. Thus, all these substances have molecular weights several times greater than the average molecular weight of the liquids in which they dissolve. The increase is relatively higher at higher temperatures than at lower temperatures. The resulting improvement in VI is not linearly proportional to the concentration.[11]

2.1.3 Pour Point

The temperature at which the oil will flow under standard test conditions is reported in increments of 5oF or 3oC as the oil pour point. For motor oils, a low spill point is very important for easy starting and proper lubrication for starting on cold days.

There are two sorts of pouring focuses, consistency pouring point, and wax pouring point. The thickness pour point is continuously drawn nearer as the temperature diminishes and the consistency of the oil increments until it does not stream beneath standard test conditions. The wax pour point happens abruptly as the paraffin wax precious stones accelerate from the arrangement and the oil cement.

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pour point depressant add do not prevent crystallization of waxy solids, but rather prevent crystal growth by coating the microcrystals during their formation; It has been suggested that these additives may also inhibit the uptake of liquid component particles, a process that was developed to explain certain aspects of spill point lubricant behavior. The additives usually consist of two general aromatic types - paraffin wax thickening products, and alkyl methacrylate polymers, which also act as VI enhancers, but some vinyl esters and alkylating polystyrenes have also been proposed [3]. A related test is the (cloud point) which decides the temperature at which wax or other solids start to partitioned from the arrangement. For paraffinic oils, usually the beginning temperature of paraffin wax crystallization [8].

2.1.4 Oxidation Resistance

Tall temperatures experienced in inner combustion motor operation advance the fast oxidation of engine oils. Usually particularly genuine for the oil coming in contact with the cylinder heads where temperature can run from 260 to 400 ^{o}C (500 to 750 oF). Oxidation causes the arrangement of coke and varnish-like asphaltic materials from paraffin-base oils and slugs from naphthenic-base oils [9].

Antioxidant added substances, such as phenolic compounds and zinc dithiophosphates, are included in the oil mixes to stifle oxidation and its impacts [11].

2.1.5 Flashpoint

The flashpoint of oil has small importance concerning motor execution and serves primarily to grant a sign of the source of the oils within the mix, for example, whether it could be a mix of tall and moo consistency oils to deliver a middle of the road viscosity or is comprised of a mix of center-cut oils[12].

2.1.6 Acidity

The erosion of bearing metals is generally due to corrosive assaults on the oxides of the bearing metals 9. These natural acids are shaped by the oxidation of lube oil hydrocarbons beneath motor working conditions and by acids created as byproducts of the combustion prepare, which are presented into the crankcase by cylinder below-by. Engine oils contain buffering materials to neutralize these destructive acids. More often than not, the dispersant and cleanser added substances are defined to incorporate soluble materials, which serve to neutralize the corrosive contaminants. Lube oil mixing stocks from paraffinic unrefined oils have great warm and

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oxidation steadiness and display lower acidities than do oils from naphthenic rough oils. The neutralization number is utilized as the degree of the natural corrosiveness of oil, the higher the number the more prominent the sharpness [9].

2.2 Lubricating Oil Additives (LOAs)

Straight mineral oils, along with compounded oils, were once able to meet all typical oil prerequisites of car and mechanical hone. As these necessities have gotten to be more serious with the dynamic improvement of motors and common apparatus it gets to be vital, to begin with, to make strides in the quality of greasing up oils by modern strategies of refining and in the long run to utilize (added substances) either to strengthen existing qualities or to bestow extra properties [1]. In the early days of their use additives were regarded with suspicion - an oil that needed an additive was necessarily an inferior oil; today additives are an accepted feature of lubricants - as of other petroleum products - and most lubricants now contain one or more additives [13].

Additives are substances that, in small quantities from a few parts per million to a few percent- confer specific properties on the lubricant [1]. The progressive increases in the severity of engine operating conditions for motor oils have made necessary the use of chemical additives. These are employed for the following specific purposes [7].

- To improve flow properties by lowering solidification temperature; decreasing change of viscosity with a change of temperature.
- To improve lubricating action by providing greater oiliness; decreasing metal wear; furnishing better film strength.
- To provide greater chemical stability by inhibiting oxidation; neutralizing oxidation promoters; inhibiting bearing metal corrosion; preventing sludge and varnish deposition.
- To preserve engine surfaces from rusting and corrosion.
- To prevent oil foaming during use.

3. Experimental work

3.1 Materials: Table (1) materials used for the preparation of Nano additive copper oxide (CuO).

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Table (1) materials used for the preparation of Nano additive copper oxide (CuO)

Material	Chemical formula	Molecular weight (g/mol)
Copper Nitrate	$Cu(NO_3))_2$.3H2O	241.60
Sodium Hydroxide	NaOH	39.99
Oleic Acid	C18H34O2	282.47

Table (2) properties of oil – stock

Specification	ASTM method	60 stock
Kin. Viscosity at 40 °C , cSt	D-7042	64.347
Kin. Viscosity at 100 °C , cSt	D-7042	8.417
Viscosity Index	D-7042	100.1
Density at 15 °C , g/cm3	D-7042	0.8827
Pour point, °C	D-97	-12
Flashpoint, °C	D-92	220

3.2 Preparation of Nano additive copper oxide (CuO)

This study contains one type of nanoparticle, which can be used as additives in the engine oil to improve its tribological properties using the precipitation method because it's a simple, low-cost method. [7]. Two solutions are prepared for the synthesis of copper oxide in Nano size. The first solution is copper nitrate; the second is a 0.1 M solution of NaOH which slowly dropped under stirring at a temperature of 80 oC until pH reach 14.

The black precipitate will appear and then be filtered and washed with distilled water. After that, the final precipitate is dried at 80oC for 16 h and calcined at 500^{o}C for 4 h. The final product is characterized by X-ray diffraction (XRD), Atomic force microscopy (AFM), Surface area (BET) and pore volume, and FTIR.

3.3 Preparation of blending

The blending was prepared by mixing (0.1, 0.5, 1&1.5) g of nano additives copper oxide material with 100 ml of 60 stock (base oil) maintaining weight by weight. CuO was added to 10 g of oleic acid by a mechanical stirrer for 10 minutes before blending with base oil. The

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blend was stirred by sonication for 20 minutes with 60% frequency, energy 1000 j, and temperature below 70^o C.

4. Results and Discussions

The final nano lubricant consists of the main base oil, nanomaterial, and surfactant. All these component shows distinguished properties such as stability and improving physical properties leading to anti-friction effects. All these compensations are occupied between the interface surface area inside the tool. These results are in good agreement with previous studies as in [13]

Some modified and enhanced mechanism has been proposed for copper oxide nanoparticles base oil, such as viscosity index, stability, and flashpoint.

The dispersion of CuO nanoparticles is achieved by ultrasound technique giving good existence forming no clusters in suspension according to Brownian motion as mentioned in[14] leading to reduce real contact area and friction boundary layer.

4.1 Characterization of nano additive copper oxide CuO

Several techniques were used to characterize the final nano-sized copper oxide particles.

4.1.1 XRD Analysis

The XRD patterns of synthesized CuO nanoparticles are shown in Figure (1) and confirm the formation of the monoclinic phase. The characteristics peaks located at 2θ= 32.583o, 35.476o, 38.977o, 48.749o [5].[9].

The crystallinity of the synthesized CuO has been calculated by considering the ratio of the sum of the 3 major peaks intensities of the prepared sample to that of standard giving a good crystallinity of 93.63 %.

Table (3) Experimental XRD data of the three strongest peaks for synthesized CuO nanoparticles and crystallite size

Peak No	2 theta	I / II	FWHM	Calculated crystallite size nm Scherrer eq
1	35.537	100	0.621	16.27
2	38.997	85	0.680	13.92
3	48.789	21	0.852	14.33

The calculated crystalline size using the Scherer equation is listed in Table (3), the average crystallite size is 14.33 nm for the final synthesized CuO nanoparticles.

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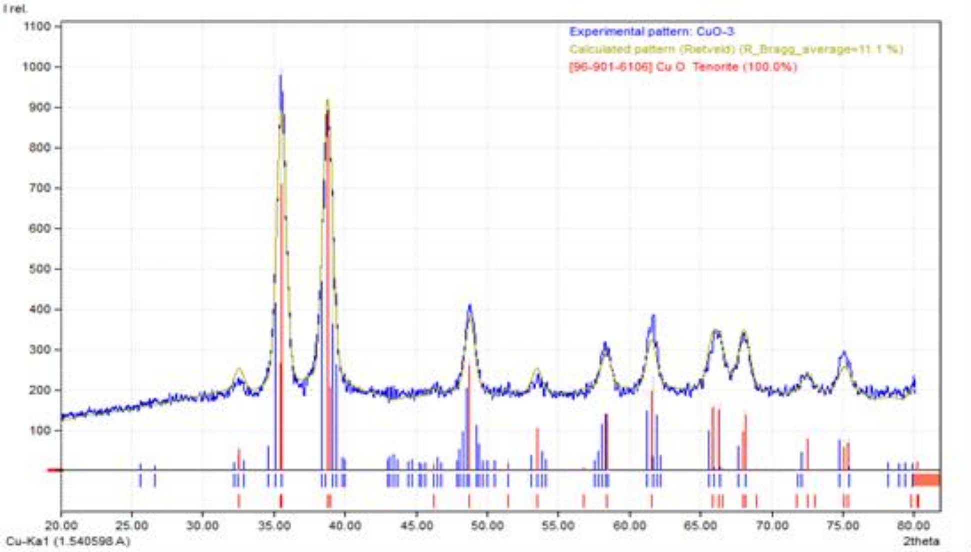

Fig. (1) XRD patterns of synthesized CuO nanoparticles.

4.1.2 AFM

Nano-sized particle conformity is done by using atomic force microscopy. The average particle size is 31.76 nm as shown in Figure (2).

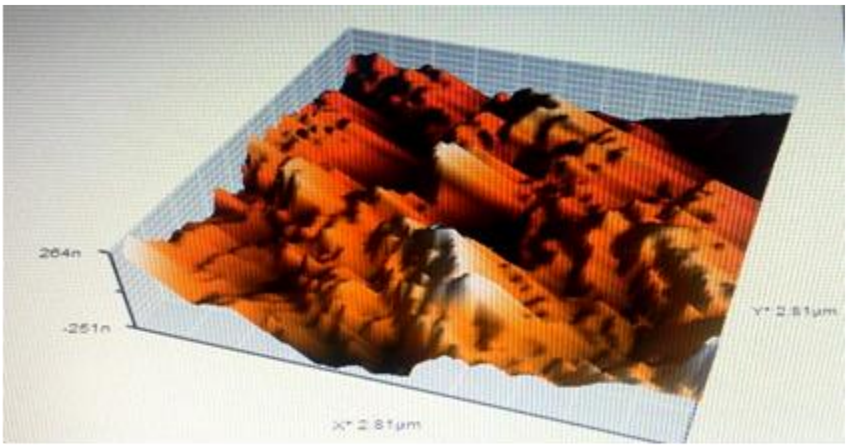

Fig.(2) 3D surface characterization of nano additive copper oxide

4.1.3 BET

Surface area and pore volume are measured according to BET method ISO 9277-2010. As shown in Table (4).

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Table (4) Properties of prepared nano additive CuO

Property	Value
Surface area, m2/g	27.6
Pore volume, cm3/g.	0.01
Pore size,nm	1.8

4.1.4 FTIR

The FTIR spectrum of CuO (Fig.3) shows the bands around 522.5 cm-1 which can be assigned to the vibration of the CuO bond. The absorption at 1634 cm-1 is attributed to (H-O-H) bending. as a result of the high surface to volume of the nanostructure, the absorption peak at 3444.13 cm-1 due to (O-H) stretching caused by adsorbed water molecules. [5], [8].

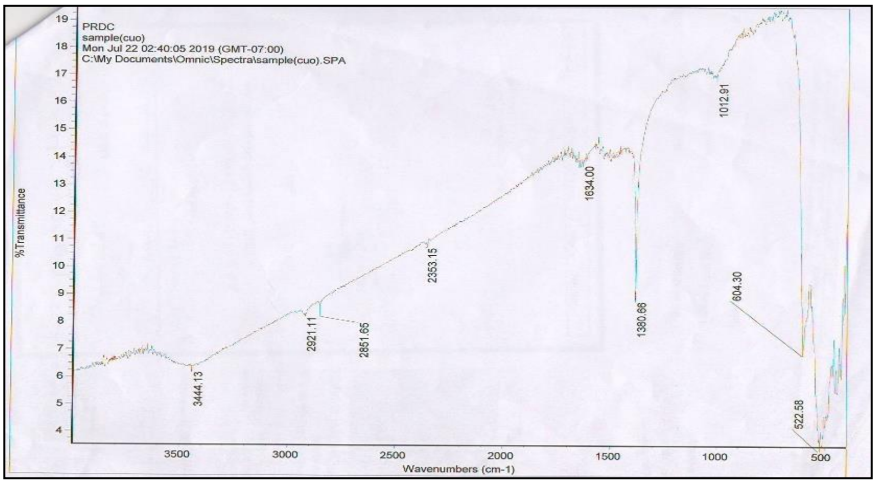

Fig. (3) FTIR spectrum of CuO

4.2 Studying of physicochemical parameters of engine oil and modified engine oil

The modified engine oil was observed after keeping undisturbed for 3 weeks. No precipitation was observed showing the stability of engine oil with nano additive.

- **Kinematic viscosity:** viscosity is one of the important properties of any lubricant. it determines the film formation tendency of the lubricant. viscosity measured at 40 and 100 o C as shown in Fig.4 .there is slight a decrease of viscosity when adding the nano additive CuO because of the weakness of interparticle and intermolecular adhesion force at a rising temperature from 40 to 100 oC. Oleic acid is added as a surfactant agent to obtain more efficient dispersed CuO particles inside the base oil phase giving a good distribution and stability with no sedimentation effects. [5],[11][15]

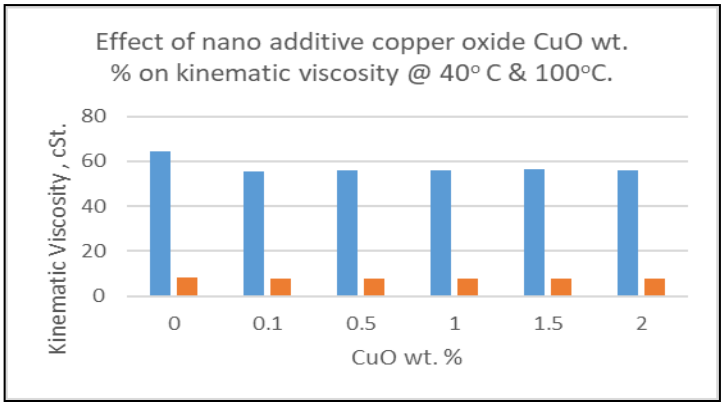

Fig. (4) Effect of nano additive copper oxide CuO wt.% on kinematic viscosity @ 40 and 100 ^{o}C

- **Viscosity index**: Higher viscosity index indicates higher film stability at higher temperatures. By adding nano additive CuO the viscosity index was increased from 100 to 110. this was due to the fact of increasing the concentration of nanoparticles the internal shear stress of lubricant increased giving better film-forming tendency at 1.5wt.% of CuO. As shown in Figure (5). [5] [16].

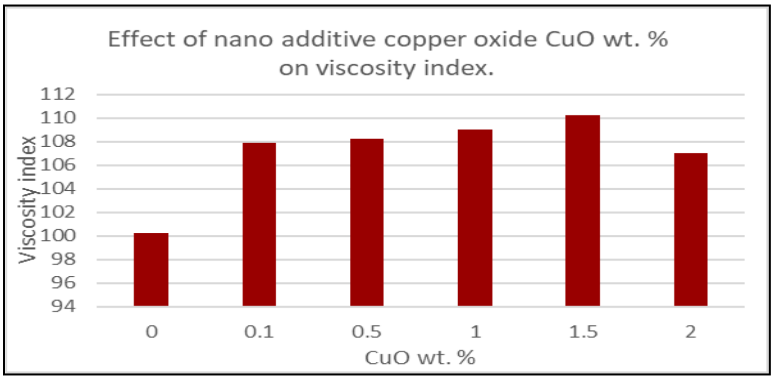

Fig. (5) Effect of nano additive copper oxide CuO wt.% on viscosity index.

- **Pour point**: there is no change in pour point when adding the nano additive CuO and the value was -12 ^{o}C. As shown in Figure (6). [12].

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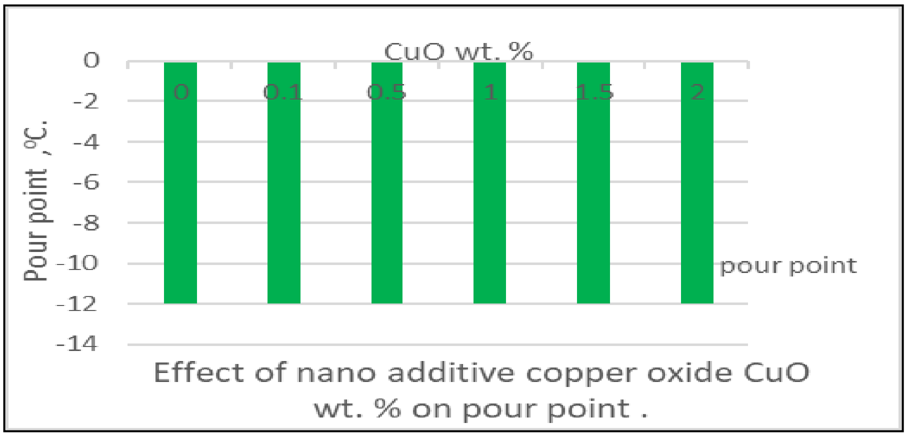

Fig. (6) Effect of nano additive copper oxide CuO wt. % on pour point.

- **Flashpoint**: the flashpoint was increased by increasing the nana additive CuO wt.%. The value increased from 220 to 240 °C, this increase is due to the rise of thermal conductivity and also it can be said that it helps the oil to resist ignition. This indicates that the modified engine oil can work as good oil even at a higher temperature condition of a different engine. As shown in Figure (7). [5], [16].

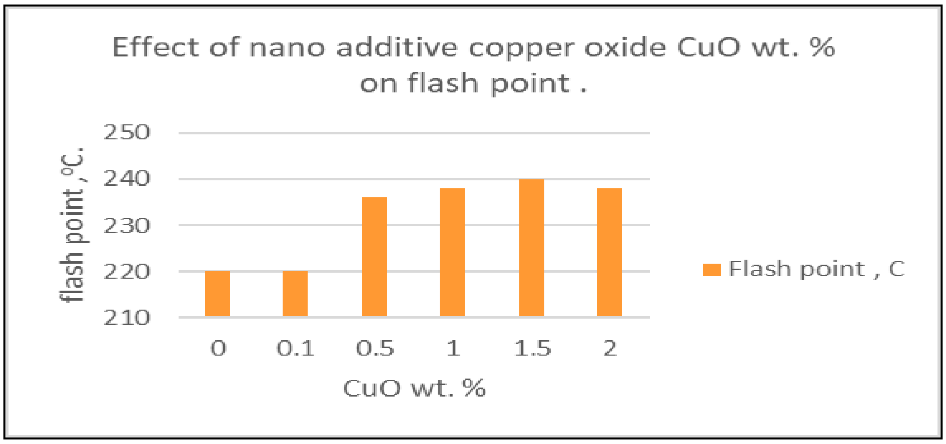

Fig. (7) Effect of nano additive copper oxide CuO wt.% on flashpoint.

- **Density**: the density was increased by increasing the nano additive copper oxide wt.% CuO as shown in Figure (8).

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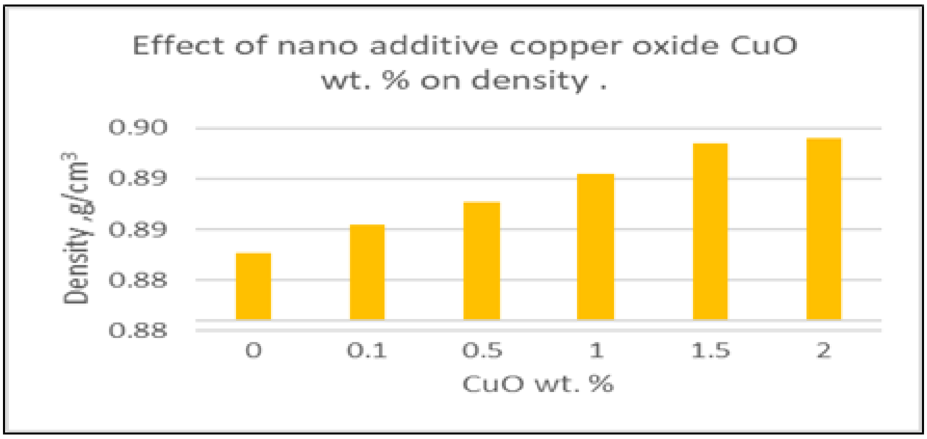

Fig. (8) Effect of nano additive copper oxide CuO wt% on density.

5. Conclusion

The following point can be concluded from the present work:

- Nano additives copper oxide has been successfully prepared with 31.76 nm.
- Viscosity index increased from (100-110) with increasing of nano additive copper oxide CuO wt. %.
- Flashpoint increased from (220-240) with increasing of nano additive copper oxide CuO wt. %.

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