ISSN: 0974-5823 Vol. 7 No. 3 March, 2022

International Journal of Mechanical Engineering

A Review of Nano Additives Used in Lubricants to Improve Tribological Performance

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Abstract:

This article deals with the prose review of the nano lubricants mixed with different base oils. The synthesis of a few of the nanoparticles and their effect on friction and wear has been analyzed. The characterization has been studied by different methods like Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Energy Dispersive X-ray Spectroscopy (EDX) It has been studied that the optimum concentration of the nanoparticles in the base oils has given significant improvement in the friction co-efficient, scar diameter, and the increase in the life of rubbing components. Nanocomposites in base oils are promising since they increase tribological features and still they are eco-friendly.

Keywords: Tribology, Friction, Wear, Nanoparticles

Introduction

Friction reduction has been a challenge to mankind. Research is being done by many scholars to minimize friction. In the beginning, water was used as the lubricant, which later emerged as natural oils for the contact surfaces. "Tribology" is the foundational science for current knowledge of friction, wear, and lubrication. The word tribos indicates rubbing motion in Greek. One-third of the fuel energy is needed to reduce friction in the tires, brakes, engine, and transmission system, the energy loss is greater in passenger cars. Only 21.5 percent of the fuel energy is used to drive a passenger automobile [1]. In comparison, fuel loss due to friction is quite significant [2,3]. Lubrication is cri

tical in reducing frictional losses at mechanical contact surfaces. It will be utilized not only to reduce wear and friction but also to prevent rust and dust by serving as an insulator revolution. Lubrication is the most effective technique for reducing energy consumption and increasing the efficiency of industrial equipment. Because most industrial machines have steel/steel contact surfaces, mineral oils, and vegetable oils were first employed as lubricants to prevent mechanical sliding components from friction and wear. Due to changing environmental conditions, bio-lubricant oils were developed that were renewable, non-toxic, non-polluting, less expensive than synthetic oil, and biodegradable [4,5]. However, manufactured synthetic oil (Group IV) PAOs are widely used in automobiles for continual improvement of lubricating performance. Synthetic oils can function under extreme cold and heat, and they have a high load-bearing ability [6]. The metallic contact surfaces are not smooth on a microscopic level, resulting in heat generation after prolonged movement. The heat generated by the rubbing motion leads the mated components to fail mechanically. Because of their excellent anti-wear properties and the ease with which they can be grafted on a shearing surface and tweaked aspiration to form a protective layer on the surface, nanoparticles have been used as lubricating oil additives to withstand this high temperature and pressure and to eliminate undesirable phenomena [7-10]. A tiny amount of nanoparticles added to the base oil can enhance tribological characteristics such as friction and wear when compared to pure base oil [11]. Nanoparticles are chosen based on their synthesis technique as well as other criteria such as lubrication, shape, size, morphology, and procedure [12-15]. The chain of nanoparticles combines to create a bigger cluster, which falls owing to gravity. Because low dispersion stability leads to sedimentation and blockages, this dispersion stability is more desired for improved lubricant performance [16]. A dispersion agent is used to decrease it.

Lubricant classifications:

Lubrication is necessary to reduce friction between moving components. It helps to smooth out the machine's operation and reduces the heat and wear generated by friction. Sliding, rolling, and fluid friction are the most common types of friction found on moving machine parts. When two sliding contact surfaces travel over each other, sliding friction develops. A roller/wheel glides freely across a surface in rolling friction. Fluid friction can occur when moving parts are near one another over a fluid. Compared to sliding friction, rolling and fluid friction are frictionless because the roller's contact area with the surface is less. They can protect moving surfaces from dirt and corrosion-causing pollutants. Fresh lubricant tends to wash away dirt and impurities when it travels between moving surfaces. Solids, semi-solids, and liquids are the three kinds of lubricants. Liquid lubricants are oils that come in a variety of forms. Semi-solid materials are gel-like substances that minimize friction between moving surfaces. Powdered solid lubricant materials are utilized to produce a thin layer that protects against damage during relative motion. Bio-lubricants (vegetable and animal oils), mineral, and synthetic oils are the three types of liquid lubricants available. Bio-lubricants are regularly utilized.

Mineral and synthetic oils, on the other hand, have mostly supplanted it. Animal lubricants are produced from animal fats such as beef, sheep, pigs, and lard. It is thought that animal fats can be soft or hard. Vegetable oils, such as castor oil and coconut oil, are lubricants produced from plants and seeds. Mineral oils are made from refined crude oil and are petroleum products. Mineral oils are more stable and perform better in terms of lubrication than bio-lubricants. Mineral oils have varied molecular sizes. Synthetic oils, on the other hand, are oils that are manufactured and have consistent molecular sizes. These synthetic oils have improved lubricating qualities, such as high pressure and temperature resistance, as well as a high load-carrying capability. Fig 1 shows the categorization of lubricating oils [17-20].

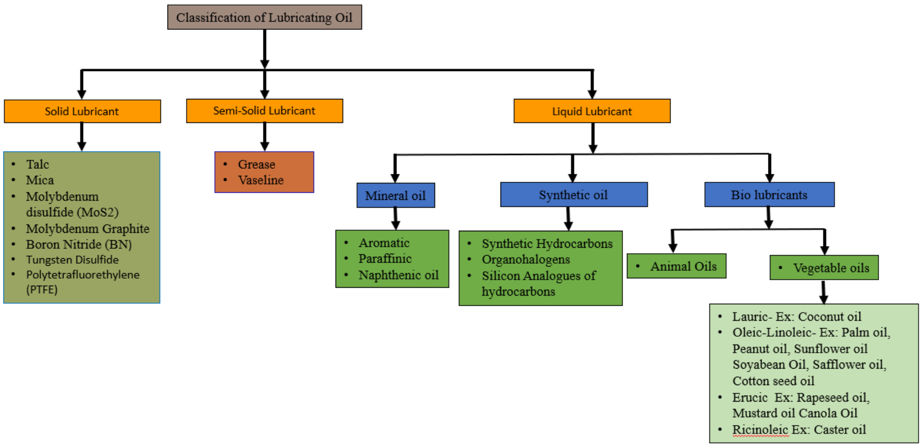

Fig 1. Classifications of lubricating oil

Nanoparticle Synthesis Techniques: There are two methods for synthesizing nanoparticles: the top-down approach and the bottom-up approach. The bulk materials are split into micron sizes and fragments are reduced to nano-dimensions in the top-down method, resulting in nanoparticles. The bottom-up technique involved taking atom-sized precursors, assembling them to produce needed nano-dimensional materials, and then sizing them to the desired size of nanoparticles. The nanoparticles are produced by machining and etching in the top-down technique, which requires some physical and chemical processes [21].

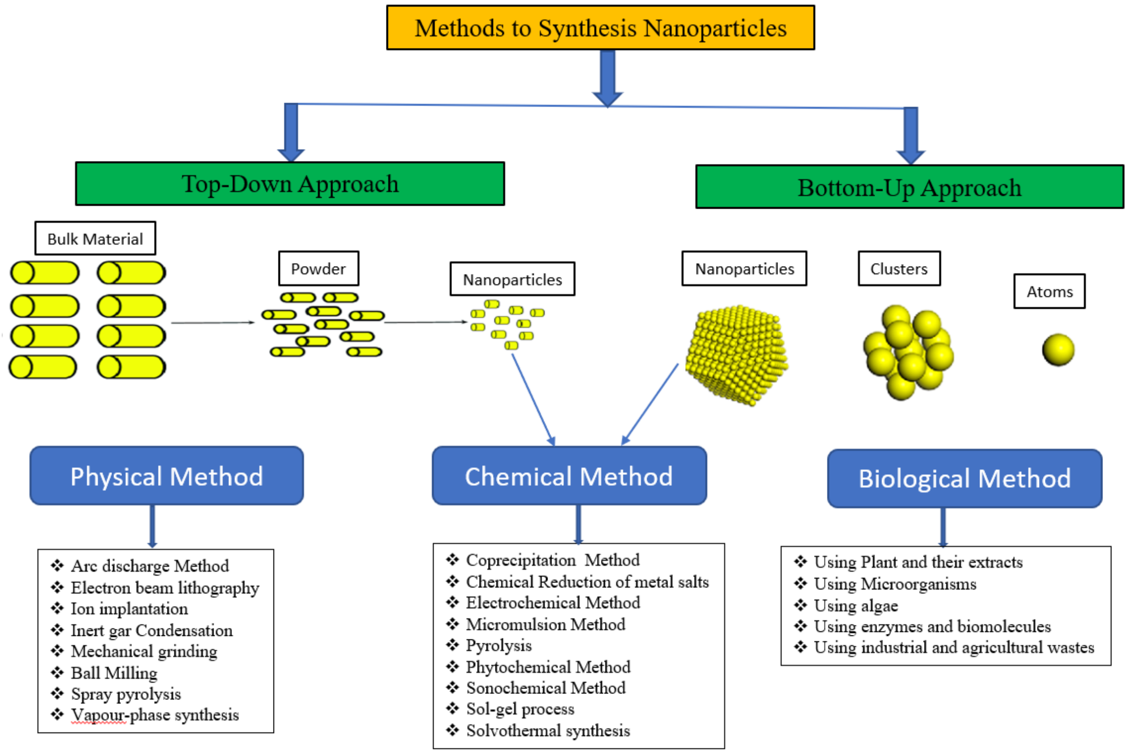

Fig 2. Synthesis Techniques for Nanoparticles

The Importance of Nanoparticle Characterization: Nanoparticle characterization is essential in the field of nanoparticles. Because of their unique morphological characteristics, size and shape are two of the most important factors to consider while characterizing nanoparticles. Researchers may also examine the surface chemistry and assess the size distribution, degree of aggregation, interfacial properties, and surface area. Furthermore, after nanoparticles have been synthesized, their crystal structure and chemical composition are extensively investigated as a preliminary step. There were no specific techniques for accomplishing this goal before today. Reliable and credible measuring methods for nanoparticles will have a significant impact on their adoption in commercial applications while also allowing the industry to meet standards. Nevertheless, because of the interdisciplinary nature of the field, the lack of suitable reference material for the calibration of analytical tools, and the difficulties associated with sample preparation for analysis and data interpretation, there are significant challenges in the analysis of nanomaterials. such as measuring their concentration in situ and online, particularly in scaled-up manufacturing, and analyzing them in complicated matrices [22].

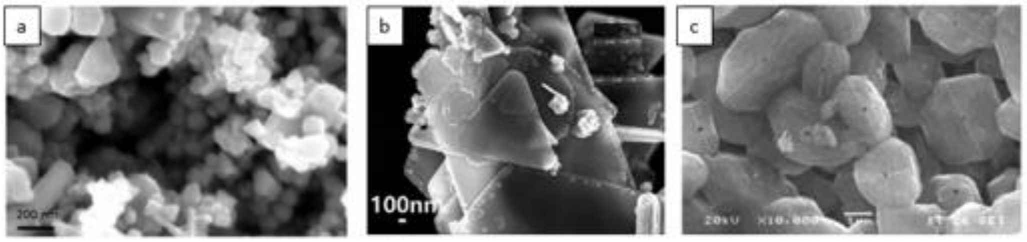

Fig 3. SEM Images of Copper nanoparticles with various shapes, sizes [23-25]

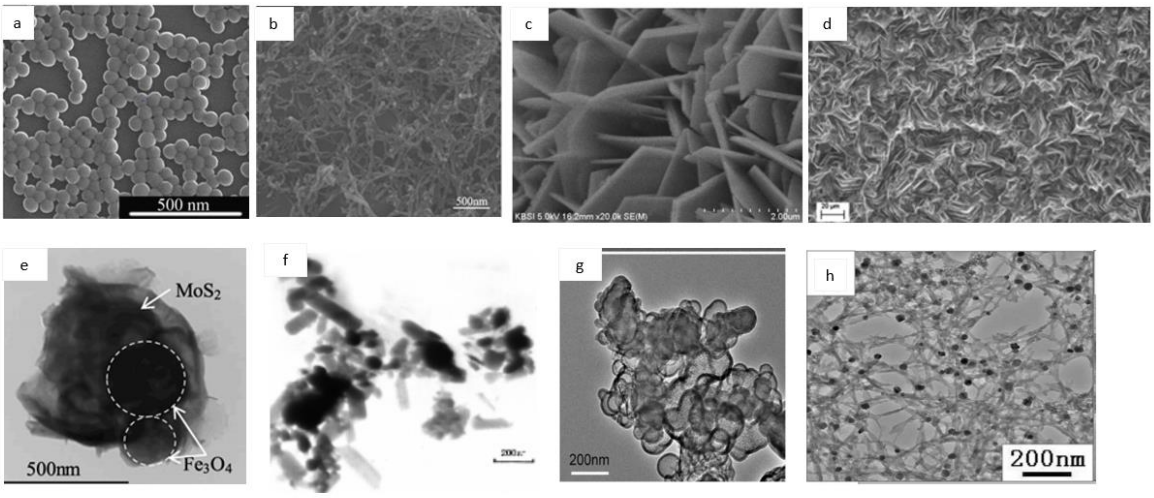

Fig 4. SEM images of a) modified Al2O3/TiO2[50] b) SOCNTs@MoS2 composite [61] c) ZnMn2O4/ZnFe2O4 nanocomposites [62] d) Cu-CeO2 nanocomposites [54]

& TEM images of e) Fe3O4@MoS2 nanocomposites f) P/Cu Nanocomposite g) BN/calcium borate nanocomposites h) Cu/SiO2 nanocomposites

Dispersion mechanism of nanoparticles in lubricants:

Because of their high specific surface area and surface energy, nanoparticles are prone to agglomeration. In the meantime, adequate nanoparticles dispersion in base oils is required for effective and stable lubrication. Mechanical stirring and the application of chemical modifiers are two common dispersion technologies devised to make them stable in liquid hydrocarbons.

Where, ϕ denotes the nanoparticles volumetric concentration ratio in the utilized base fluid, which has the following definition [65]:

$$\Phi=\frac{\frac{m\,nano}{\rho\,nano}}{\frac{m\,nano}{\rho\,nano}+\frac{m\,oil}{\rho\,oil}}$$

ρ nano –Density of nanoparticles

ρ oil- Density of oil

For better dispersion of the Taguchi method to operate, the experimental results must be converted into a signal-to-noise (S/N) ratio. The terms signal and noise refer to the desired and unwanted output characteristic values, respectively. The ratio is a metric for determining how far quality attributes stray from expected values, which are split into three categories: low, high, and normal is better. Because the smallest size of aluminium nanoparticles in liquid paraffin is crucial in this research, a low-is-better feature is sought. As a result, the S/N ratio will take the following form:

$\frac{S}{N}=-10\log\left(\frac{1}{n}\sum_{i=0}^{n} y_i^2\right)\mathrm{dB}$

The S/n ration is stated on a decibel(dB) scale, where n is the number of experiments and y_i is the response of each experiment. S/N rations are calculated by replacing them with an equation from data about nanoparticle size [10].

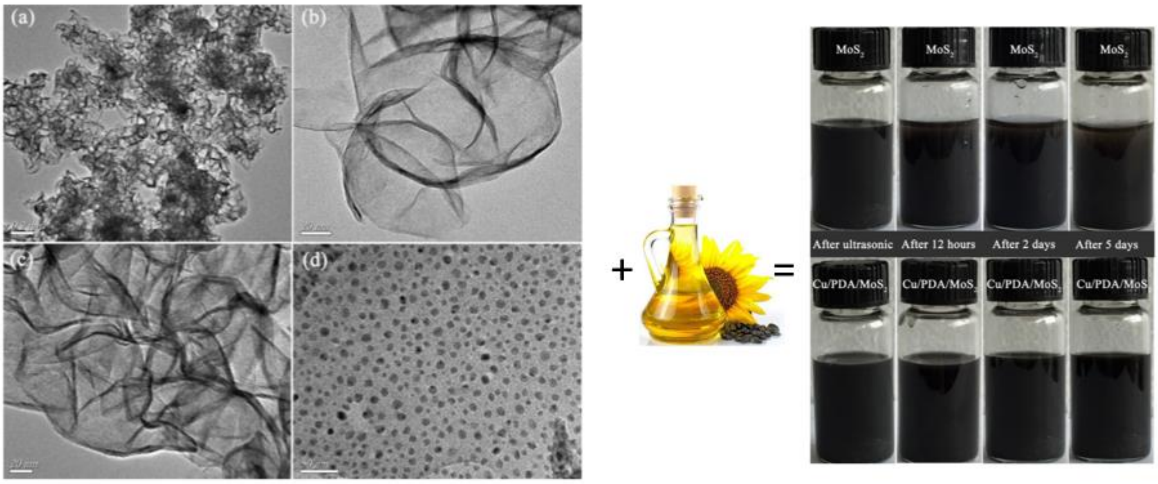

Fig 5: TEM images of nanosheets a&b) MoS_2 c) PDA/MoS_2 and d) Cu/PDA/MoS_2 at different magnifications plus sunflower oil gives nano lubricants with good dispersion [56]

Nano lubricants having a base oil and dispersed nanoparticles developed as a new type of nano lubricant. Nanoparticles can be described in a variety of ways when mixed with base oil. Because nano lubricants take so long to stabilize, researchers proposed methods for assessing dispersion during this time. On the other hand, the agglomeration of nanoparticles in the base oil is a stumbling block to further development. The majority of studies used ultrasonic dispersion to reduce agglomeration and sedimentation. Because of the size and shape of nanoparticles, if the nanoparticle size is small, the nanoparticle with base oil disperses uniformly. When the size of nanoparticles grows larger, sedimentation occurs at the base oil's bottom. Coupling agents are employed to avoid this.

The diffusion point of copper nanoparticles has lowered dramatically due to the nano-scale impact, as revealed by heating simulation experiments. As a result, the heat generated during friction is most likely causes the accumulation of copper nanoparticles, which therefore leads to the so-called repairing effect [26].

The importance of nanoparticle size in tribology: The size of nanoparticles has a major impact on the tribological properties of nano lubricants in many ways. Because of their small size, nanoparticles may infiltrate the contacting surface and reduce friction and wear processes [26-28,66]. When choosing the size of the nanoparticle's material, the root means square roughness of the lubricated surface must be taken into account. These metallic surfaces are not smooth at the microscopic level, but rather feature numerous peaks and throughs known as asperities, which cause damage to the system and often lead to mechanical failure when such microscopic peaks make contact. Hundreds of billions of nanospheres infiltrate the gap between metal surfaces. The spheres' spherical morphology allows them to roll on the spot and act as nano ball bearings, lowering frictional forces. The nanoparticle's capacity to exfoliate allows them to cling to the surface and smooth out any forming a protective film on the moving metal surfaces. This known as a tribo film inhibits wear and provides the metal with long-term protection and the capacity to endure high pressure. Whereas if the particle size is excessively large in comparison to the space between the asperities, the larger particles will be deposited on the contact surface, resulting in poor lubrication. The size of nanoparticles can also influence the lubricant's homogeneity.

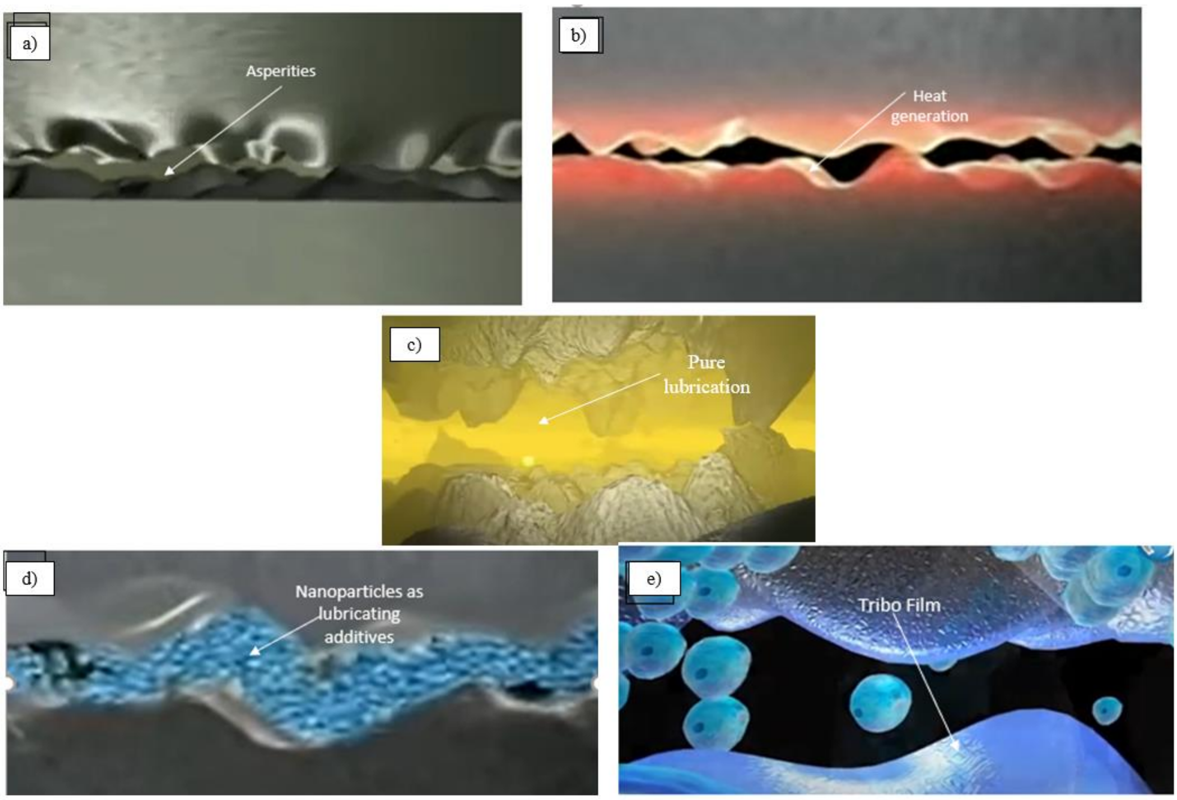

Fig 6: Tribo film formation between asperities in microscopic level using nanoparticles as lubricating additives

The rubbing surfaces without lubrication in fig 6 (a)&(b) show that there was a certain heat which was generated between the mating surfaces, as a result of which those surfaces got melted and thus friction is generated. In fig 6(c), when pure sunflower oil was added as lubrication in between the parts the surface life was increased to a certain extent. But in fig 6(d)&(e), with the addition of nanoparticles and nanocomposites, there was a protective layer known as tribo film was formed between the mating parts and thus decreased the wear& friction co-efficient

Lubricant	Nanoparticles	Shape & Size (nm)	Characterization	Method of dispersion and duration(min)	Tribology test	The optimum composition of nanoparticles with a base oil (wt.%)	Remark	Ref
Tetrabutyl ammonium acetate	Pd	2	Optical Microscope & XRD	----	Ball-On-Disk	2.0	Enhance tribological properties	27
TBA & Paraffine	Pd	Spherical (2)	SEM, TEM & EDX	---	Ball-On-Disk tribometer	5.0	Enhanced load carrying capacity and reduce the shear strength and wear rate	28
PAO6	Ni	20	SEM & EDS	Ultrasonic probe (30)	Block on ring	1.0	Wear reduction 7-30% Friction reduction 5-45%	29
PAO6	Ni	7.5,13.5 and 28.5	TEM XRD & FTIR	Ultrasonic irradiation	Four ball Machine	0.05	At 7.5 nm WSD were reduced compared to 13.5 and 28.5nm with 0.05 wt.%	30
Mineral-based oil	Bi	7-65	SAXS	Magnetic string (30-40)	Four ball tester	---	Approximately 16% of reduction in friction and wear	31
PAO6	Carbon coated Cu	25	SEM and EDS	Ultrasonic probe (30)	Block and ring, four ball testers	0.5	50% wear reduces	32

Pongamia oil	Cu	25-85	Optical microscope	Ultrasonication Technique	Pin-On-Disk tribometer	0.075	Minimizing wear and WSD	33
Lithium grease	Cu	Triangular (50-100)	SEM & TEM	Triple roller mill Homogenised	Ball On Disk Tribometer	0.5	12% of friction reduction, 82.2 % wear losses were reduced	34
Mineral oil SAE 10	Fe, Cu, and Co	Cu (50-80)	SEM	CEWLS	Four ball testers	0.5	11% Co,23%(Fe) and 47%(Cu) were reduced wear. 20%(Co), 39%(Fe), and 49% (Cu) were minimized friction	35
Engine oil	Cu	80-120	AFM including XPS	----	Pin-On-Disk & Thrust roller bearing	3.0	Reduces friction and wear	36
Raw oil		25 and 60	SEM, AFM & EDS		Disc-on-Disc tribometer	0.1	Friction reduces to 44-39%	37
50CC oil		20	TEM, SEM, EDS, XPS	Ultrasonic dispersion	Four-Ball tester	0.2	The copper film is formed between 2 frictional surfaces, separating them and preventing direct contact. Enhancing the elastic deformation of the contact surfaces minimize wear and reduces friction.	64
Paraffin oil	Al	65-85	SEM & EDS	Ultrasonic Stirring (30)	Ball-On-Ring	0.5	Improves the tribological properties	38

Lubricant	Nanoparticles	Shape & Size (nm)	Characterization	Method of dispersion and duration(min)	Tribology test	The optimum composition of nanoparticles with a base oil (wt.%)	Remark	Ref
Mineral oil	CuO	Nearly Spherical 30-40	SEM & UV Visible Spectroscopy	Ultrasonic Shaker (30)	Pin-On-Disc tribometer	1.0	Reduces friction up to 50%	39
Paraffin oil	CuO	Nearly Spherical 50	SEM	Ultrasonic bath (60)	Four ball tribo machine	0.2	Enhance the lubricating properties	40
Plam kemel oil	CuO	Spherical 40	SEM & EDX	High shear homogenizer (40)	Pin-On-Disk	0.34	Reduced WSD up to 48% & COF 56%	41
Water-based lubricant	CuO	Spherical 20	SEM	Homogenously dispersion after surface modification of water-based lubricant	Four ball testers	0.2	Friction minimizes up to 69.2% and wear 55.1%	42
Lubricating oil	Al_2O_3	Spherical 78	SEM & EDS	Ultrasonication (30)	Four ball tester and Trust ring tribometers	0.1	Reduced COF in four-ball tester 17.6%, WSD 41.75% whereas COF in trust ring tribometer 23.92%	**43**
Water-based lubricant	TiO_2	Round 20	TEM & XRD	Ultrasonic string (10)	Ball-on-disk tribometer	0.8	Friction reduces to 49.5% and wear 97.8%	**44**
Mineral oil	TiO_2	Round 20-25	SEM, TEM, XRD, FTIR, and Raman spectroscopy	Mechanical stirrer (15)	Reciprocating Pin-On-Disc	0.25	Reduced coefficient of friction	**45**
Engine oil	TiO_2	10-25	----	Ultrasonic Shaker	Pin-On-Disc tribometer	1.5	Nanoparticles are multifunctional additives and enhance the tribological properties	**46**
Plam oil	TiO_2	22.98		Ultrasonic Bath (30)	Four ball tribo machine	0.1	Reduces friction and wear	**47**

Liquid paraffin	SiO_2	Spherical 58	**FE-SEM FT-IR EDS,**	Ultrasonic stirring (60)	Ball-on-ring tester	0.05-0.5	Compared to pure liquid paraffin, 0.05-0.5 SiO_2 Wt.% have improved tribological properties in terms of load-carrying capacity, Anti-wear and friction reduction	**66**

Table1: Characterization of various lubricants with nanoparticles

Lubricant	Nanocomposites	Shape & Size (nm)	Characterization	Method of dispersion and duration(min)	Tribology test	Optimum composition of nanoparticles with a base oil (wt.%)	Remark	Ref
Lubricating oil	Al_2O_3/SiO_2	Elliptical 70	Infrared Spectroscopy & metallurgical Microscope	Dispersed ultrasonically (30)	Four ball tester & Thrust-ring test	0.5	The Al_2O_3/SiO_2 nanocomposites might provide a rolling action between rubbing surfaces, changing the friction condition from sliding to rolling. As a result, the friction coefficient has decreased	**48**
Lubricating oil	Al2O3/TiO2	Spherical 75	SEM & EDS	Ultrasonication (30)	Four ball tester & Thrust-ring test	0.1	Due to a Chemical reaction, a tribo-boundary film formed. So, significantly COF and WSD reduced	**49**
Base oil	ZrO_2/SiO_2	Spherical	SEM, XRD & EDS	ultrasonic for 30	Four ball tester & Thrust-ring test	1.0	An anti-wear layer developed and the COF was decreased by 21.14 percent in four-ball tests using ZrO2/SiO2 composites. Coming to the thrust-ring causes very little wear.	**50**
Lubricating oil	ZrO_2/SiO_2	50 to 80	TEM	Ultrasonic (30	Four ball tester & Thrust-ring test	0.1	COF was lowered by 16.24 percent, while vertical WSD was reduced by 14.59 percen t, improving tribological cha racteristics.	51
CD15W-40 lubricating oil	Serpentine/La(OH)$_3$ composite	Granular 50	SEM, XRD &TEM	Ultrasonic probe for (5) Agitator (30)	Multi-functional friction abrasion tester and Ring-block wear tester	---	It shows friction-reduction, anti-wear, and self-repair capabilities. COF is lowered by 24.63 percent, while friction spot diameters are reduced by 41.88 percent.	**52**
Lubricating oil	Palygorskite/Copper	Clubbed 200	SEM and EDX	Ultrasonically oscillated (30)	Abrasive-Wear Tester	---	When compared to P nanoparticles and without lubricant additives, the wear mass loss of the nanocomposites is reduced by 41.7 percent and 63.2 percent, respectively, under the test circumstances. The friction coefficient of nanocomposites reduces by 44 percent when compared to no lubricant additives, but just slightly when compared to P nanoparticles and produces self-repair film on the contact surfaces.	**53**

--	Cu-CeO_2	Globular (20-60)	SEM and EDX	---	Ball-on-disk wear	---	Enhances the tribological properties	**54**
--	Al/Al_3Fe	Nanocrystalline (57)	XRD, SEM & TEM	---	Pin- on-disk	0.1	The composite's mechanical properties improve as the weight percent Al_3Fe concentration rises, and they are comparable to those of other traditional composites. The wear qualities enhance as the amount of the dispersed phase, Al3Fe, rises, but the wear rate rises for all compositions as the load increases.	**55**
Sunflower Oil	Cu@MoS_2	Valley (8~13)	EDS &XPS	Ultrasonication (30)	Ball on Disk	0.5	When 0.5 wt percent Cu/PDA/MoS_2 nanosheets were introduced to sunflower oil, the friction coefficient and wear scar width were reduced by 37.8 percent and 28.5 percent, respectively. The Cu/PDA/MoS_2 nanosheet's tribological characteristics are good.	**56**
PAO6	Mn_3O_4@G	Nanosheets	TEM, XRD, Raman Spectra & FIB	Self-Dispersion	Reciprocating sliding tribometer	0.075	The friction coefficient and wear depth were lowered by 75 percent and 97 percent, respectively. When compared to base oil at an ultralow concentration (0.075 wt percent) and a high temperature of 125ºC	**57**
Soybean Oil	Cu/PDA/GO	---	TEM, EDS, XRD, FTIR & Raman Spectra	Self-Dispersion	Ball on Plate	0.1	Under the sliding circumstances, Cu/PDA/GO nanocomposites had the lowest friction coefficient. The wear scar on the steel disc indicated that Cu/PDA/GO nanocomposites outperformed Cu nanoparticles, GO, and Cu/GO nanocomposites in terms of anti-wear performance.	**58**
palm trimethylolpropane (TMP) ester	TiO_2/SiO_2	Nearly Spherical (50)	SEM, EDX & AFM	Ultrasonic Probe (30Min)	Four-Ball tester & Piston Ring-Cylinder liner sliding tester	0.75	Nano-TiO2/SiO2 demonstrated significant dispersion capabilities, particularly at a concentration of 0.75 wt percent. Compared to blank palm (TMP) ester, such homogeneous dispersion provided a stable suspension and reduced friction and wear. Under high-pressure settings and piston ring–cylinder liner contact, palm (TMP) ester supplemented with 0.75 wt percent nano-	**59**

							TiO_2/SiO_2 showed better tribological properties.	
Bio-Diesel &Aqueous medium	Fe_3O_4/MoS_2	30-60	TEM, EDS & XRD	--	Four-Ball tribometer	1.2	When lubricated with Fe_3O_4/MoS_2 in bio-diesel oil and aqueous medium, the friction and WSD decreased by 34.6 percent and 29.7 percent, respectively	**60**
Dibutyl Phthalate (DBP)	SOCNTs/MoS_2		SEM, EDX, XRD, Raman Spectroscopy	Ultrasonically (30)min	Four-Ball Tribometer	0.02	The DBP with 0.02 wt. percent SOCNTs/MoS_2 composite had the best tribological performance, with a 57.93% reduction in COF and a 19.08 % reduction in WSD	**61**
PAO4	$ZnMn_2O4/ZnFe_2O4$	Nano flanks (50-125)	SEM, EDX	Ultrasonically (30min)	Four-ball tester	1.0	Improves the lifetime of the matting parts.	**62**
PAO6	RGO/Fe_3O_4	---	TEM, XPS, Raman Spectra, SEM, Laser images	Ultrasonically treated (1hr)	CETR-UMT tribometer	0.1	In addition, the average wear volume of steel disc fell by 52.27 percent RGO/Fe_3O_4 ratio of 0.1 wt. percent. This acts as a protective coating between friction pairs, which reduces the wear.	**63**

Table 2: Characterization of various lubricants with nanocomposites

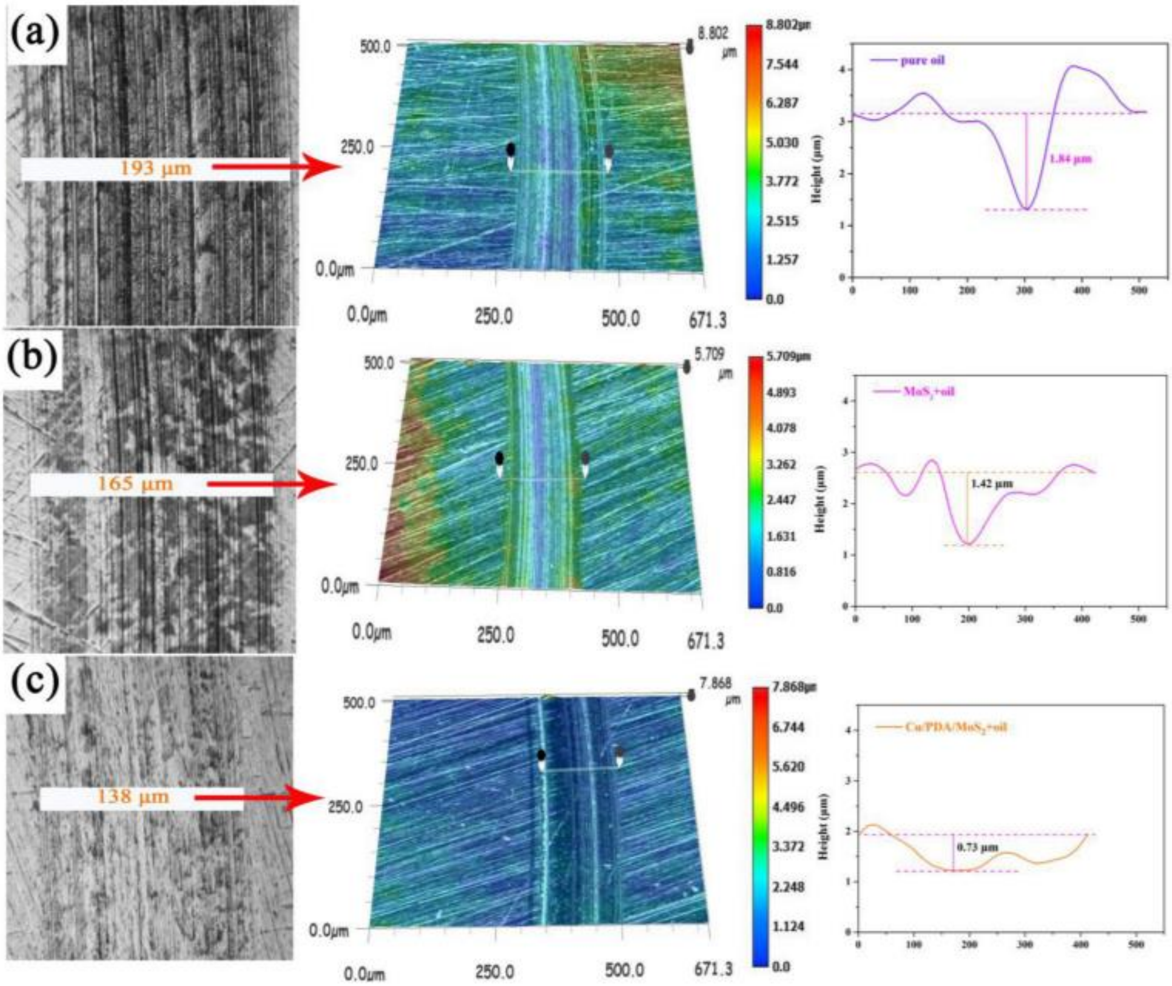

Fig 7: Optical micrographs and three-dimensional profiles of wear tracks on steel disks (Load: 5N, Speed: 300r/min, Time: 30. min) a) pure sunflower oil b)1.0 wt percent of MoS_2 nanosheets and c) 0.5 wt percent of Cu/PDA/MoS_2 nanosheets [56].

In Fig 7, With sunflower oil alone, the wear track on the ball was 193µm in width,7(a). With the addition of 1.0wt% of MoS_2 nanosheets in the base oil, the wear was 165 µm,7(b) but the nanocomposites showed more efficient values than pure and nanoparticles in the base oil.0.5wt% of Cu/PDA/ MoS_2 nanosheets exhibited very less wear track of 138 µm,7(c) which showed that nanocomposites are more lubricating in nature between the mechanical mating Components.

Conclusion:

This article exposes the exclusive evaluation of the use of various nano additives for lubrication. The synthesis and characterization of nanoparticles in different shape sizes and based on the method of preparation were analyzed. Nano Particles in the base oil gave improved results than the pure base oils exhibited. But the nanocomposites in the lubricant showed promising results improving the tribological properties thus increasing the life of the mechanical parts.

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