

Evaluation of Physico-Chemical and Tribological Properties of Engine Oil Dissipated with Titanium Dioxide Nanoparticles

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Abstract—The physicochemical and tribological properties of HP Racer 4 engine oil dissipated with inorganic nanoparticles such as TiO₂ were evaluated using a Four Ball Tester. Samples are prepared by dissipating the nanoparticles in engine oil at different weight percentages. These nanoparticles are made stable in the lubricant by adding CTAB as a surfactant. The stability of the lubricant with nanoparticles dissipated in it is evaluated by studying its ultraviolet-visible spectra. Using a Four Ball Tester, the anti-wear and anti-friction properties of the samples are tested, and an evaluation of the TiO₂ nanoparticles with surfactants CTAB is done to compare their relative performances. Lubricants' friction and wear characteristics dissipated with nanoparticles vary based on the load applied. It is observed that there is a significant reduction in the coefficient of friction when the base oil is dissipated with TiO₂ nanoparticles. The results obtained from this investigation will be used to develop new and efficient lubricants for automotive engine applications

Key words— Tribology, Nanoparticles, Lubricant, Friction, Wear, Four Ball Tester, Viscosity Index, Total Base Number.

I. INTRODUCTION

Tribology is the science and engineering of interacting surfaces in relative motion. It includes the study and application of friction, wear, and lubrication. Since the 1990s, new areas of tribology have emerged, including nano tribology, bio-tribology, and green tribology. These interdisciplinary areas study the friction, wear, and lubrication at the nano scale. Development of new materials such as copper initiated the development of fundamentally new approaches in the lubrication field. One of the main reasons for the frequent change of car engine oil is that it becomes contaminated with hard debris particles that can wear out the engine components. The selection of the best lubricant and understanding the mechanism by which it acts to

separate surfaces in a bearing or other machine components is a major area for study in tribology.

The tribological interactions of a solid surface's exposed face with interfacing materials and the environment may result in a loss of material from the surface. The process leading to the loss of material is known as "wear". Major types of wear include abrasion, friction (adhesion and cohesion), erosion, and corrosion. Wear can be minimized by modifying the surface properties of solids by one or more of "surface engineering" processes (also called surface finishing) or using lubricants (for frictional or adhesive wear).

Friction is the force resisting the relative motion of solid surfaces, fluid layers, and material elements sliding against each other. When surfaces in contact move relative to each other, the friction between the two surfaces converts kinetic energy into thermal energy (i.e., it converts work to heat), for example, when a viscous fluid is stirred. An important consequence of friction can be wear, which may lead to performance degradation and/or damage to components.

Lubrication is the process or technique employed to reduce friction between and wear of one or both surfaces in proximity and moving relative to each other, by interposing a substance called a lubricant in between them. The lubricant can be solid (e.g., copper, TiO₂), a solid/liquid dispersion, a liquid such as oil or water, a liquid-liquid dispersion (grease), or gas. With fluid lubricants, the applied load is either carried by pressure generated within the liquid due to the frictional viscous resistance to motion of the lubricating fluid between the surfaces or by the liquid being pumped under pressure between the surfaces.

Adequate lubrication allows smooth continuous operation of equipment, reduces the rate of wear, and prevents excessive stresses or seizures at bearings. When lubrication breaks down, components can rub destructively against each other, causing heat, local welding, destructive damage, and failure.

A lubricant, either solid or liquid, creates a separating film between surfaces of adjacent moving parts to minimize direct contact between them, decreasing heat caused by friction and reducing wear, thus protecting the engine. Apart from reducing friction and wear, a lubricant performs other diverse functions which help protect and prolong the life of the equipment. A lubricant acts as a heat sink and dissipates the heat, decreasing the possibility of deformation and wear due to thermal loading. It also facilitates the smooth operation of the equipment by removing and suspending potentially harmful products such as carbon, sludge, dirt, and wear debris. The lubricant also prevents metal damage from corrosion wear due to oxidation products. Engine oil or engine lubricant is any of various substances that are used for the lubrication of internal combustion engines.

Corrosion prevention is achieved by the formation of a physical film on metal surfaces that resists oxygen, water, and acids. The addition of anti-friction and anti-wear additives into lubricating oil to reduce friction and wear or to mend a worn surface has been widely applied in lubrication engineering for quite a long time. Any machine in which one material slides or rubs over another is affected by complex tribological interactions, whether lubricated or unlubricated. All modern machines require the use of a lubricant to prevent metal-to-metal contact, which leads to the generation of frictional heat and wear. The wear rate in equipment depends upon the degree of the metal-to-metal contact. High-speed, low-load operation leads to lower wear than slow-speed, high-load operation. A layer of lubricant that eliminates surface contact virtually eliminates wear and decreases needed power by one-third.

1.1 Lubricant

A lubricant is a substance introduced to reduce friction between surfaces in mutual contact, ultimately reducing the heat generated when the surfaces move. It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the

surfaces. The property of reducing friction is known as lubricity. In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats are used in frying pans and in baking to prevent food sticking), biomedical applications on humans (e.g., lubricants for artificial joints), ultrasound examination, medical examinations, etc.

Typically, lubricants contain 90% base oil (most often petroleum fractions, called mineral oils) and less than 10% additives. Vegetable oils or synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons, and many others are sometimes used as base oils. Additives deliver reduced friction and wear, increased viscosity, improved viscosity index, resistance to corrosion and oxidation, aging or contamination, etc. Non-liquid lubricants include grease, powders (dry graphite, PTFE, molybdenum disulfide, tungsten disulfide, etc.), PTFE tape used in plumbing, air cushions, and others. Dry lubricants such as graphite, molybdenum disulfide, and tungsten disulfide also offer lubrication at temperatures (up to 350 °C) higher than liquid and oil-based lubricants are able to operate. A good lubricant generally possesses the following characteristics:

- High boiling point and low freezing point (in order to stay liquid within a wide range of temperature)
- High viscosity index
- Thermal stability
- Hydraulic stability
- Demulsibility
- Corrosion prevention
- High resistance to oxidation

1.2 Classification of Lubricants

A lubricant is a substance that reduces friction and wear at the interface of two materials. The lubricant at the interface reduces the adhesive friction by lowering the shear strength of the interface. Based on the shear strength of the lubricant or molecular state, lubricants are classified into four categories:

- Gaseous lubricants
- Liquid lubricants
- Semi-solid lubricants
- Solid lubricants

1.2.1 Solid Lubricants

A solid lubricant is basically any solid material that can be placed between two bearing surfaces and which will shear more easily under a given load than the bearing materials themselves. The coefficient of friction in dry lubrication is related to the shearing force and the bearing load. The two primary property requirements of solid lubricants are:

The lubricant must be able to support the applied load without significant distortion, deformation, or loss in strength.

The friction coefficient and the wear rate must be acceptably low.

1.2.2 Liquid Lubricants

Liquid lubricants reduce friction and wear between two moving or sliding metallic surfaces by providing a continuous fluid film in between them. They act as a cooling medium, a sealing agent, and a corrosion preventer. Liquid lubricants are classified into many types, depending on the type of base oil used, which include vegetable oil and animal oil, mineral oil from petroleum and blended oil, doped oil, or compound oil. There are two systems for oil classification: the SAE (Society of Automotive Engineers) viscosity grade and the API (American Petroleum Institute) classification that designate the type of engines for which the oil was designed. When classifying winter oils, the SAE viscosity grade is the "W" number. In general, the lower the first number, the better the oil performance in extremely cold conditions. Conversely, the higher the second number, the better the oil protection at higher temperatures. The API designation is typically "S" designation for gasoline engines and a "C" designation for diesel engines. Most of today's oils carry an SH, CF, or SJ, CF designation signifying that they are suitable for all gasoline or diesel automotive applications.

1.2.3 Semi-Solid Lubricants: Grease

Grease is a black or yellow sticky mass used in the bearings for lubrication. Lubricating greases consist of lubricating oils, often of quite low viscosity, which have been thickened employing finely dispersed solids called thickeners. It consists of base oils (75 to 95%), additives (0 to 5%), and minute thickener fibers (5 to 20%). Different types of base oil may be used in the manufacture of grease, including petroleum (naphthenic, paraffinic) and synthetic (PAOs, esters,

silicones, glycols). The viscosity of the base oil is the most significant property. Lighter, lower viscosity base oil is used to formulate low-temperature greases, while heavier, higher viscosity base oil is used to formulate high-temperature greases. Chemical additives are added to grease to enhance their performance. Performance requirements, compatibility, environmental considerations, color, and cost all factor into additive selection. Solid lubricants such as graphite, TiO₂ nanoparticles, and EP additives are a few examples.

1.2.4 Gas Lubricants

Gas (i.e., Air, Nitrogen, and Helium) lubrication is used for ultra-thin film thickness (separation) between tribo-pairs. This type of lubrication can be used in a temperature range of -2000 °C to 20000 °C. No vaporization, cavitation, solidification, or decomposition occurs using gas lubricants. It also has very low viscosity (1000 times less viscous than even the thinnest mineral oil), thus providing ultra-low friction and usage at high speeds. The load capacity of gaseous lubricants is very low. These lubricants also have low-damping features and ultra-low film thickness.

1.3 Additives in Lubricants

To prevent failure, engine oils and gear oils are dispersed with extreme pressure (EP) and anti-wear (AW) additives that react chemically with the metal surfaces, forming easily sheared layers and thereby preventing severe wear and seizure. Gear oils use two main types of EP additives: those that are temperature-dependent and those that are not. The most commonly used additives are temperature-dependent additives like boron, chlorine, phosphorus, and sulfur. These elements react with the metal surfaces due to extreme temperatures caused by high operating loads and form new compounds on the surface, such as iron chlorides, iron phosphides, and iron sulfides. These metal salts produce a chemical film that acts as a barrier to reduce friction and wear and reduce the possibility of welding.

II. PROCEDURE

2. NANOPARTICLES

Many researchers have tried to improve the tribological characteristics of lubricants to decrease friction coefficients and wear rates. One approach is

simply using additives in the base lubricant to change its properties. Recently, nanoparticles have emerged as a new kind of additive because of their size, shape, and other properties.

2.1 Definition

Nanoparticles are generally defined as particulate matter with at least one dimension less than 100 nm. Any nanoparticle will have an exceptionally high surface area to volume ratio; this is one of the reasons for some of their unusual properties. However, this high surface area also means that the surface of any given nanoparticle is an important material component. So, even the simplest nanoparticle will have a surface chemistry that is distinctly different from that of the core material.

2.2 Structure and Shape of Nanoparticles

A nanoparticle can be split into two or three layers: a surface that may often be functionalized, a shell material that may be intentionally added, and a core material. Often, nanoparticles are only referred to by their core material because this is the part of the nanoparticle that results in key properties for most applications. Nanoparticles can be of various shapes like spherical, rod, hexagonal, flower-type, layered, or platelet-type hexagonal, etc. Previous studies have been conducted on spherical nanoparticles, but it has been experimentally proven that flower-type nanoparticles reduce friction to a greater extent. Engine oil containing the TiO₂ nanoparticles nanomaterials penetrate more easily into the interface space and form a continuous film on the surface. Nanoflowers are rounded and loosely connected to each other with a narrow size distribution. The nanoflowers have a well-defined shape and are uniform in both morphology and particle size distribution.

2.3 Properties of Nanoparticles

The main parameters of interest concerning nanoparticles are:

Physical Properties: Size, shape, specific surface area, aspect ratio, Agglomeration/aggregation state, Size distribution, Surface morphology/topography, Structure, including crystallinity and defect structure, Solubility

Chemical Properties: Structural formula/molecular structure, Composition of nanomaterial (including

degree of purity, known impurities or additives), Phase identity, Surface chemistry (composition, charge, tension, reactive sites, physical structure, photocatalytic properties, zeta potential), Hydrophilicity/lipophilicity

With the increasing number of newly emerging manufactured nanomaterials, the importance of the potential dissolution kinetics needs to be emphasized. Since dissolution kinetics is frequently proportional to the surface area, nanomaterials are likely to dissolve much more rapidly than larger-sized materials. Nanoparticles often have unique physical and chemical properties. For example, the electronic, optical, and chemical properties of nanoparticles may be very different from those of each component in the bulk. At the nanoscale, materials behave very differently compared to larger scales, and it is still very difficult to predict the physical and chemical properties of particles of such a very small size. Nanoparticles can be encountered as aerosols (solids or liquids in air), suspensions (solids in liquids), or as emulsions (liquids in liquids). Due to the high surface area/volume ratio, the following properties become size-dependent. Thus, nanoparticles possess unexpected properties like:

Chemical properties like reactivity, catalysis

Thermal properties like melting temperature

Mechanical properties like adhesion, capillary forces

Optical properties like absorption and scattering of light

Electrical properties like tunneling current, conductivity

Magnetic properties like the super paramagnetic effect

III. MATERIALS AND METHODS

3.1 Surfactants

Surfactants play an important role as cleaning, wetting, dispersing, emulsifying, foaming, and anti-foaming agents in many practical applications and products, including paints, emulsions, adhesives, inks, biocides (sanitizers), shampoos, kinds of toothpaste, firefighting (foams), detergents, insecticides, deinking of recycled papers, ski waxes, and spermicides (nonoxynol-9). “Surfactant” is a contraction of the three words “Surface Active Agents.” Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between a liquid and

a solid. Generally, any material that affects the interfacial surface tension can be considered a surfactant, but in the practical sense, surfactants may act as wetting agents, emulsifiers, foaming agents, and dispersants. Surfactants tend to reduce the surface tension of a liquid where they are dissolved. Surfactants like Sorbitan Monooleate (SPAN-80) and Cetrimonium Bromide (CTAB) are used to bind the nanoparticles of materials like graphene which provide a lubricating film to increase the lubricating effects of engine oil.

In the bulk aqueous phase, surfactants form masses such as micelles, where the hydrophobic tails form the core and the hydrophilic heads are immersed in the surrounding liquid. Other types of structures can also be formed such as spherical micelles or lipid bilayers. The shape of the molecules depends on the balance in size between the hydrophilic head and hydrophobic tail. A measure of this is the HLB, Hydrophilic-lipophilic balance. Higher HLB surfactants (>10) are hydrophilic (“water-loving”) and form O/W (Oil-in-water) emulsions. Lipophilic surfactants possess low HLB values (1-10) and form W/O (water-in-oil) emulsions. Dish detergents and surfactants for emulsion polymerization are high HLB surfactants. The dynamics of surfactant adsorption is of great importance for practical applications such as in emulsifying or coating processes as well as foaming, where bubbles or drops are rapidly generated and need to be stabilized. As the interface is created, the adsorption is limited by the diffusion of the surfactant to the interface, which can result in the kinetics being limited. These energy barriers can be due to stearic or electrostatic repulsions; stearic repulsions form the basis of how dispersants function. Surface rheology of surfactant layers is important to the stability of foams and emulsions. Most surfactants' “tails” are fairly similar, consisting of a hydrocarbon chain, which can be branched, linear, or aromatic. Fluorosurfactants have fluorocarbon chains. Siloxane surfactants have siloxane chains. Recent advances in surfactant technology have seen the development of mixed chains and/or complex structures.

3.2 Sonication

Sonication can be used to speed dissolution by breaking intermolecular interactions. It is commonly used in nanotechnology for evenly dispersing

nanoparticles in liquids and has become the industry standard for:

- Dispersing
- Deagglomerating
- Particle size reduction
- Particle synthesis and precipitation
- Surface functionalization

The primary part of a sonication device is the ultrasonic electric generator. This device creates a signal (usually around 20 KHz) that powers a transducer. This transducer converts the electric signal by using piezoelectric crystals or crystals that respond directly to the electricity by creating a mechanical vibration. This vibration, molecular in origin, is carefully preserved and amplified by the sonicator until it is passed through to the probe. The sonication probe transmits the vibration to the solution being sonicated. This probe is a carefully constructed tip that moves in time with the vibration, transmitting it into the solution. The rapid movement of the probe creates an effect called cavitation. Cavitation occurs when the vibrations create a series of microscopic bubbles in the solution, pockets of space wedged between the molecules that form and then collapse again under the weight of the solution, sending out tiny shockwaves into the surrounding substance. Thousands of these bubbles forming and collapsing constantly create powerful waves of vibration that cycle into the solution. There are different-sized probe tips based on what sort of sonification process is desired. A very small tip will create excellent cavitation effects, but it will have a limited area of effect based around the probe itself. Larger tips can reach a greater quantity of the solution but will not produce such an intense reaction.

3.3 Four Ball Tester

A reduction in friction in tribological contacts will lead to reduced energy requirements. It is, therefore, important to be able to measure the frictional characteristics of various liquid lubricants. Energy and material losses occur in virtually every mechanical device in operation. When reviewed based on a single machine, these losses may seem insignificant. However, when the same losses are repeated on millions of machines, the costs become quite substantial. Lubricating oils are needed to reduce frictional losses as well as to support working load and avoid metal-to-metal contact between the components

working together for obtaining desired functions in machines. As per the American Society of Testing Materials, the standard test method for the measurement of Extreme Pressure (E.P.) properties of lubricating fluids is defined by ASTM D 2783. This test method is commonly known as the Four Ball Test.

3.4 Materials

HP Racer 4 Engine Oil

Titanium Oxide Nanoparticles (TiO₂)

CTAB Surfactant

Distilled Water

3.5 Preparation of Lubricant Samples

The TiO₂ nanoparticles were dispersed in the engine oil (HP Racer 4) at different weight percentages (0.1%, 0.2%, and 0.3%) with the help of CTAB as the surfactant. The mixture was then sonicated for 2 hours to ensure uniform dispersion of the nanoparticles in the oil.

3.6 Stability Test

The stability of the prepared lubricant samples was evaluated by measuring their ultraviolet-visible spectra over a period of time. A stable dispersion will show minimal changes in the spectra over time.

3.7 Viscosity Test

Viscosity is defined as the resistance of a fluid to flow. The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. Viscosity is a property arising from collisions between neighboring particles in a fluid that are moving at different velocities. When the fluid is forced through a tube, the particles which compose the fluid generally move quickly near the tube's axis and slowly near its walls; therefore, some stress (such as a pressure difference between the two ends of the tube) is needed to overcome the friction between particle layers to keep the fluid moving. Viscosity is one of the most important properties of a fluid and plays a very prominent role in the petroleum industry. The viscosity of a crude oil affects our ability to pump it out of the ground; the viscosity and volatility of a fuel affect how easy it is to atomize in the fuel injector; the viscosity of a lubricant affects its ability to protect an engine. Viscosity of a liquid can be mentioned in two ways: Kinematic viscosity and Dynamic viscosity. Both represent the same property of a liquid as the

ratio of dynamic viscosity and kinematic viscosity is the density of that liquid.

3.7.1 Viscosity Index

Viscosity index (VI) is an arbitrary measure for the change of viscosity with variations in temperature. The lower the VI, the greater is the change of viscosity of the oil with temperature and vice versa. VI is used to characterize viscosity changes with relation to temperature in lubricating oil. The viscosity of liquids decreases as temperature increases. The viscosity of a lubricant is closely related to its ability to reduce friction. Generally, the least viscous lubricant which still forces the two moving surfaces apart is desired. If the lubricant is too viscous, it will require more energy to circulate.

3.7.2 Test Method (ASTM D 445-06)

Kinematic viscosity was determined using ASTM D 445-06. About 20 ml of the sample was poured into the U-tube viscometer, which was placed in a water bath at a constant temperature of 40°C. The time taken for the sample to flow between two marked points on the tube was measured, and the kinematic viscosity was calculated using the formula:

$$\text{Kinematic Viscosity (cSt)} = k \times t$$

Where:

k = viscometer constant

t = flow time in seconds

3.8 Total Base Number Test (TBN)

Total Base Number (TBN) is a measurement of basicity that is expressed in terms of the equivalent number of milligrams of potassium hydroxide per gram of oil sample (mg KOH/g) that is required to titrate and neutralize the acidic components in a sample. TBN generally ranges from 6–80 mg KOH/g in modern lubricants, 7–10 mg KOH/g for general automotive use, and 10–15 mg KOH/g for diesel operations. TBN is typically higher for marine-grade lubricants, approximately 15–80 mg KOH/g, as higher TBN values are designed to increase the operating period under harsh operating conditions before the lubricant requires replacement. The TBN value of oil will gradually drop over time as an engine is operated, so routine testing for TBN can provide useful information about the serviceability of the oil and an early warning of developing corrosion problems. TBN can also be a particularly useful tool in assessing the

combustion efficiency of an engine. If rapid depletion is observed, fuels containing a higher amount of impurities such as sulfur have a greater potential for forming sulfuric acid, which would decrease the TBN sooner. ASTM D2896 – 07 is the standard test method used to measure the Base Number of Petroleum Products by using Potentiometric Perchloric Acid Titration. This test method is applicable to both fresh oils and used oils, where the only difference is the mixtures of solvents used to pre-dissolve the oil sample.

3.9 Friction Test and Wear Test

The friction and wear properties of the lubricant samples were evaluated using a Four Ball Tester according to ASTM D 4172-94. The test involves rotating a steel ball on three stationary steel balls under a specific load and speed for a specific duration. The wear scar diameter on the stationary balls and the coefficient of friction are measured.

IV. LITERATURE REVIEW

- The application of nanofluids in several engineering practices is gaining paramount importance, and in the literature, many studies related to nanotribology can be found.
- Nano-scale metal particles, which enjoy tiny size (less than 100 nm) and other special physical properties, have drawn great attention in many engineering fields, including the lubricant industry. 1
- Nanofluids may be useful as alternative coolants, greases, lubricants in automotive applications, coolants for microelectronics, and many other industries.
- Nano-sized graphene nanoparticles were studied as friction-reducing lubricant additives.
- Extensive experimentation and studies are carried out to evaluate the suitability of graphene nanoparticles as lubricant additives.
- Experimental results and SEM observations have shown a mending effect on the friction surface after being lubricated with oil-containing graphene nanoparticles.
- This chapter provides a brief survey of the literature on various techniques for improving the tribological characteristics of lubricants and decreasing the friction coefficients.
- Many researchers have tried to improve the tribological characteristics of lubricants to decrease friction coefficients and wear rates.
- Recently, nanoparticles have emerged as a new kind of additive because of their size, shape and other properties.
- A nano lubricant is a new kind of engineering lubricant made of nanoparticles, dispersant and base lubricant.
- Rapoport et al. were one of the earliest researchers to work on lubricants dispersed with transition metal sulfide nanoparticles.
- They conducted experiments to determine the wear and friction of lubricant dispersed with WS₂ and Cu nanoparticles nanomaterials.
- It was found that there is a significant decrease in both wear and friction with the dispersion of nanomaterials.
- Rapoport et al. (2002) showed that inorganic Fullerene-like (IF)-MoS nanoparticles were tested under boundary lubrication and ultra-high vacuum 2 (UHV) and were found to give an ultra-low friction coefficient in both cases compared to hexagonal (h)-MoS material.
- Work with IF-WS revealed that the benefit effect of the inorganic fullerene-like materials decreases at high loads and sliding velocities.
- Street et al. (2004) developed using carbon nano-onions as a potential additive in base lubricant Krytox 143 AB for aerospace applications.
- The lifetimes were tested in ambient air and ultra-high vacuum.
- They analyzed that these particles can provide adequate lubrication similar to graphitic material and could considerably reduce friction.
- Lie et al (2009) explained the ending effect as a lubrication mechanism.
- Under severe conditions of high temperature and load, the nanoparticles suspended in nano lubricants assemble and form clusters that maintain their spherical characteristics even if they agglomerate.
- To investigate the physical and tribological properties of nano lubricants, friction coefficients and temperatures were measured by a disk-on-disk tribometer.
- The results show that when comparing fixed plates coated with raw and nano lubricants, the

plate coated with a nano lubricant containing graphite nanoparticles had a lower friction coefficient and less wear.

- These results indicate that graphite nanoparticle additives improve the lubrication properties of regular lubricants.
- Wu et al (2008) explained how Molybdenum disulfide (Cu nanoparticles), tungsten disulfide (WS₂) and many other layered inorganic compounds were found to have a comparable structure with carbon fullerene and could form inorganic fullerene (IF)-like structures under appropriate conditions.
- Especially Wu et al (2008) explained how Molybdenum disulfide (Cu nanoparticles), tungsten disulfide (WS₂) and many other layered inorganic compounds were found to have a comparable structure with carbon fullerene and could form inorganic fullerene (IF)-like structures under appropriate conditions.
- Especially for the IF-MS₂ (M = Mo, W) materials, they showed better tribological properties compared with the regular MS₂ (M = Mo, W) powders, the main favourable benefit of the hollow WS₂ nanoparticles was attributed previously to the following three effects, namely: (a) rolling friction (b) the IF nanoparticles serve as spacer, which eliminate metal-to-metal contact between the asperities of the two mating metal surfaces and (c) third body material transfer.
- In 2014, Zhenyu J. Zhang, Dorin Simionescu and Carl Schaschke showed that the magnitude of the interactions between two surfaces mediated by a lubricant that contains hybrid nanoparticles is strongly affected by the size, aspect ratio and concentration of nanoparticles due to their enhanced steric contribution, packing efficiency and the tendency for aggregation.
- They also showed that, with the large libraries of nanoparticles, hybrid nanoparticles would find broad applicability in formulations of new types of lubricant additives for different base oils with engineered purposes without compromising the higher tolerances demanded by most high-performance machinery.
- Hou Xianjun explained in his paper in 2016 about the enhancement of the thermophysical properties (thermal conductivity and viscosity) of engine oil

using nanolubricant additives in automotive engines.

- Al₂O₃, TiO₂ and Al₂O₃/TiO₂ hybrid nanoparticles were suspended in commercially available engine oil (5W-30) at 0.25 wt% for formulating nanolubricants.
- It was observed that thermal conductivity was enhanced by a margin of 12–16% for a temperature range of 10–130 °C facilitating the dissipation of frictional heat and maintaining engine oil properties, as compared with commercial lubricants.
- The tribological tests showed a minimization of the friction coefficient and wear rate of the ring by 40–50% and 20–30%, respectively.

V. METHODOLOGY

The physicochemical and tribological properties of HP Racer 4 engine oil dissipated with inorganic nanoparticles such as TiO₂ were evaluated using a Four Ball Tester.

Samples are prepared by dissolving the nanoparticles in engine oil at different weight percentages.

These nanoparticles are made stable in the lubricant by adding CTAB as a surfactant.

The stability of the lubricant with nanoparticles dissolved in it is evaluated by studying its ultraviolet-visible spectra.

Using a Four Ball Tester, the anti-wear and anti-friction properties of the samples are tested, and an evaluation of the TiO₂ nanoparticles with surfactants CTAB is done to compare their relative performances.

The base lubricant used is Racer oil, and surfactant C-TAB was added to it.

Four ball tester to conduct friction test and wear test.

Stability test is also conducted to check the stability of the lubricant.

VI. COMPONENTS

HP Racer 4 engine oil

HP RACER 4 is a premium 4-stroke motorcycle engine oil designed for modern, geared bikes. It's formulated to meet the stringent requirements of API SL and JASO MA 2 standards. The oil offers superior

engine, clutch, and gear protection, enhancing bike performance and durability.

Key Features:

- **Premium Quality:** Made with high-grade Group II base stocks and advanced additive technology.
- **High Performance:** Meets or exceeds API SL and JASO MA 2 standards.
- **Clutch Slip Prevention:** Features CSP Technology for smooth wet clutch operation and better pick-up.
- **Durability and Efficiency:** Provides longer oil and engine life, high fuel efficiency, and lower maintenance costs.
- **Wide Application:** Suitable for various 4-stroke geared bikes from manufacturers like Hero, Bajaj, Yamaha, Honda, Suzuki, TVS, and Royal Enfield.
- **BS II-VI Compliant:** Suitable for a wide range of vehicles with different emission standards.

TiO₂ nanoparticles

TiO₂ nanoparticles are particulate matter with at least one dimension less than 100 nm. They have a high surface area to volume ratio, giving them unusual properties and a surface chemistry different from the core material.

They can be structured in two or three layers: a functionalized surface, a shell, and a core material, often referred to as the nanoparticle.

TiO₂ nanoparticles can take various shapes, including spherical, rod, hexagonal, flower-type, layered, or platelet-type hexagonal

CTAB Surfactant

Cationic surfactants are similar in nature to anionic surfactants, except the surfactant molecules carry a positive charge at the hydrophilic portion. Many of these compounds are quaternary ammonium salts as well as Cetrimonium Bromide (CTAB). These surfactants are generally used for sulphide nanoparticles like TiO₂ nanoparticles and WS₂

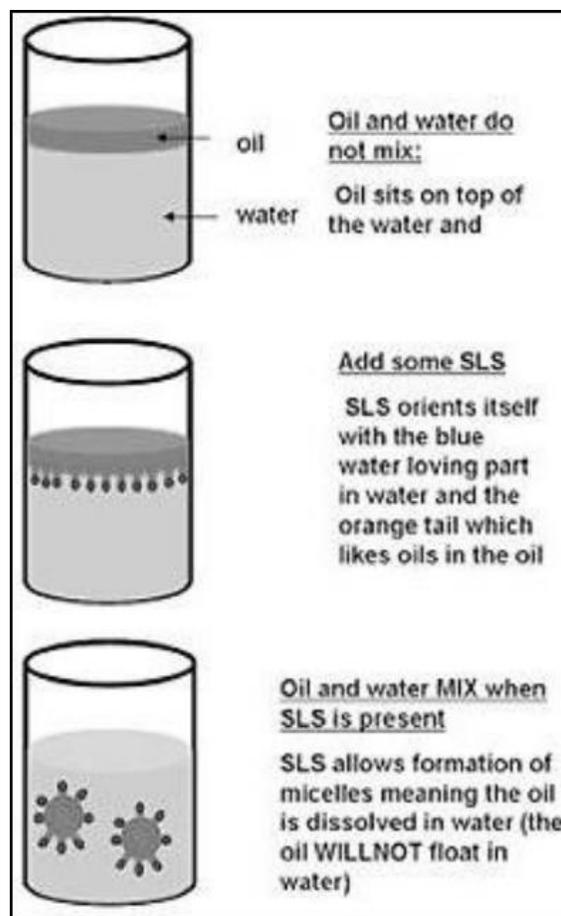


Fig: Function of surfactants

Four Ball Tester

The Four Ball Tester is used to measure the Anti-Wear (AW) and Extreme Pressure (EP) properties of grease and lubricating oil.

The test involves rotating a 12.7mm diameter steel ball under load against three stationary steel balls immersed in the lubricant. The speed of rotation, normal load, and temperature can be adjusted according to ASTM standards.

The Anti-Wear characteristics of lubricants are evaluated by measuring the wear scar diameters on the balls. The Extreme-Pressure capacity of lubricants is evaluated by measuring the normal load at which welding occurs at the contact interface.

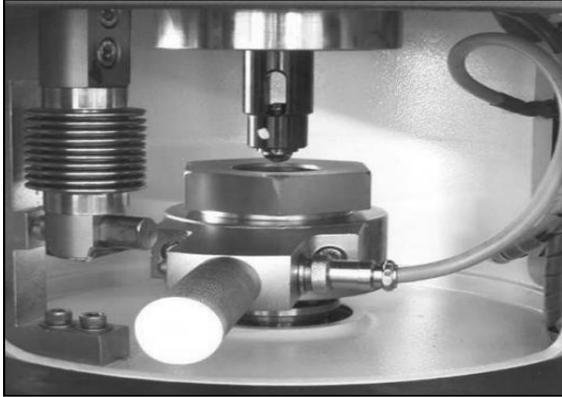


Fig: Four Ball Tester

PROCESS PARAMETERS

Nanolubricants are a novel class of lubricants engineered by dispersing nanoparticles into base fluids. These lubricants have demonstrated improved tribological properties, including reduced friction and wear, compared to conventional lubricants. Titanium dioxide (TiO₂) nanoparticles have garnered significant attention in nanolubricant research due to their unique properties, such as high surface area-to-volume ratio, chemical stability, and potential for enhancing load-bearing capacity. The preparation of stable and effective TiO₂ nanolubricants requires careful consideration of several process parameters. This document outlines the key parameters involved in the preparation process

process

The following process parameters play a critical role in determining the properties and performance of the final TiO₂ nanolubricant:

- **Nanoparticle Concentration:** The concentration of TiO₂ nanoparticles in the base lubricant is a key parameter. Increasing the concentration can enhance the tribological properties up to a certain point. However, excessive concentration may lead to increased viscosity and potential agglomeration, which can negatively impact performance. The document mentions a concentration of 0.05 wt%.
- **Surfactant Type and Concentration:** The choice of surfactant and its concentration are critical for achieving stable dispersion. Different surfactants have varying affinities for the nanoparticles and the base lubricant. The concentration must be optimized

to provide sufficient stabilization without adversely affecting the lubricant's properties.

- **Mixing Method and Parameters:** The method and parameters used for mixing, such as sonication time, stirring speed, or milling duration, significantly affect the degree of dispersion and the stability of the nanolubricant. Sufficient mixing is essential to break down agglomerates and ensure a homogeneous mixture. The document specifies sonicating the mixture for 2 hours.
- **Temperature:** The temperature during the preparation process can affect the stability and properties of the nanolubricant. In some cases, elevated temperatures may be required to improve the solubility of the surfactant or reduce the viscosity of the base fluid. The document mentions that sonication was done at ambient temperature.
- **Time:** The duration of the mixing process is another important parameter. Sufficient time is needed to ensure that the nanoparticles are well-dispersed and that the surfactant has had time to interact with the particle surfaces.



Fig: Formulation of Nanolubricants

Equipment Used

The principal equipment used in preparation of TiO₂ nano lubricant:

Probe sonicator



Fig: Set-Up for Probe sonicator

VI. RESULTS

4.1 Stability Test

The ultraviolet-visible spectra of the lubricant samples showed minimal changes over a period of 7 days, indicating that the TiO2 nanoparticles were stably dispersed in the engine oil with the help of CTAB surfactant.

4.2 Viscosity Index Test

Temperature (Centigrade)	Kinematic viscosity of Racer oil (centistokes)	Kinematic viscosity of Racer oil with 0.1% TiO2 nanoparticles (centistokes)	Kinematic viscosity of Racer oil with 0.2% TiO2 nanoparticles (centistokes)	Kinematic viscosity of Racer oil with 0.3% TiO2 nanoparticles (centistokes)
40	13	14	15	16
100	4	4.1	4.2	4.3

The viscosity index (VI) was calculated from the kinematic viscosity values at 40°C and 100°C using the following formula:

$$VI = [(L - U) / (L - H)] \times 100$$

Where:

- L = Kinematic viscosity of an oil of 0 VI at 40°C
- H = Kinematic viscosity of an oil of 100 VI at 40°C
- U = Kinematic viscosity of the test oil at 40°C

The calculated viscosity index values are:

- Racer oil: 120
- Racer oil with 0.1% TiO2 nanoparticles: 110
- Racer oil with 0.2% TiO2 nanoparticles: 100
- Racer oil with 0.3% TiO2 nanoparticles: 90

From the results, it is concluded that the value of the viscosity index is reduced when TiO2 nanoparticles are dissipated in the oil. Therefore, the oil suspended with nanoparticles is the optimal solution, and the lubricant with this respective viscosity can be forwarded for further testing.

4.3 Total Base Number Test

Oil sample	TBN (mg KOH/g)	Percentage change
TBN of Racer oil (original)	5.9	
TBN of Racer oil dissipated with 0.1% TiO2 nanoparticles	6.5	10.17
TBN of Racer oil dissipated with 0.2% TiO2 nanoparticles	6.9	16.94

| TBN of Racer oil dissipated with 0.3% TiO2 nanoparticles | 7.2 | 22.03 |

From the results, it is observed that the value of TBN is reduced when the nanoparticles are suspended in the oil. Hence, it is concluded that the oil suspended with nanoparticles is the optimal solution, and the lubricant with this respective TBN can be used for further testing.

4.4 Friction Test| S. NO | COMPOSITION | MAXIMUM LOAD, (N) | FRICTION FORCE, (N) | COEFFICIENT OF FRICTION | % CHANGE |

| ---- | ----- | ----- | ----- | ----- | ----- |
 | 1. | Racer 4 | 1275.58 | 0.5837 | 0.1286 | + 42.88 |
 | 2. | Racer4 +0.01% TiO2 nanoparticles + CTAB | 1371.06 | 0.4823 | 0.0686 | - 23.77 |
 | 3. | Racer4 +0.02% TiO2 nanoparticles + CTAB | 1466.54 | 0.444 | 0.0605 | - 31.18 |
 | 4. | Racer4 +0.03% TiO2 nanoparticles + CTAB | 1562.02 | 0.4132 | 0.0529 | - 38.60 |

The table shows a significant reduction in the coefficient of friction when TiO2 nanoparticles are added to the base oil. The reduction is more pronounced with increasing concentration of nanoparticles.

4.5 Wear Test

S.NO	Composition	Wear Scar Diameter (mm)
1	Racer 4	0.63
2	Racer4 +0.01% TiO2 nanoparticles + CTAB	0.52
3	Racer4 +0.02% TiO2 nanoparticles + CTAB	0.48
4	Racer4 +0.03% TiO2 nanoparticles + CTAB	0.45

The wear scar diameter decreases with the addition of TiO2 nanoparticles, indicating improved anti-wear properties of the lubricant.

VII. CONCLUSION

The following conclusions are arrived at based on the studies.

Nanoparticles of TiO2 dispersed in 2% weight % could improve anti-wear and anti-friction properties of HP Racer 4 oil.

Nanoparticles could be made stable in the lubricant by surface modification.

The wear scar diameter and the friction coefficient have decreased considerably when TiO₂ nanoparticles are used

Nanocomposite Reinforced with Graphene Nanoparticles

VIII. FUTURE SCOPE

The document says that Nanofluids have demonstrated the potential to be employed as substitutes for coolants, greases, and lubricants in the automotive sector, as well as coolants for microelectronics and various other industries.

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