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Nanotechnology: A Promising Tool for Lubricants

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Abstract:- Lubricant industries are focusing on biodegradable materials like modified vegetable oilsfor the production of lubricants and avoiding the conventional petroleum based lubricants. This is because of their adverse environmental effects as they contain various heavy metals and their salts likeSb_2O_3,Sb_2S_3,As_2S_2,As_2S_4,$AsCl_3$,$PbHAsSO_4$,$PbCO_3$, $HgCl_2$, Hg_2Cl_2, $Hg(NO_3)$ etc. But there is a drawback of vegetable oil based lubricants that they have a higher rate of oxidation and lower viscosity index. Thus we need to conflate some external additives to abstain this trouble. A number of natural and synthetic lubricant additives are being used since longer times to improve the performance of lubricants but natural additives have very limited properties. There are also some petroleum based additives but again they have lesser biodegradability and higher toxicity.

Nano-Technology based lubricant additives are not only eco-friendly but also used in traces unlike the conventional petroleum based lubricant additives. They are helpful in improving the thermal as well asoxidative stability, viscosity index, dispersion properties, better anti-wear characteristics, high biodegradability and various other physicochemical properties.

This review paper encompasses various methods of production of biolubricants, importance of lubricant additives, their methods of synthesis, characterization, properties and advantages of nano lubricant additives over conventional petroleum based additives. Various methods of production of nano-lubricant additives, their properties and their effect on the performance on lubricityand their comparison with conventional petroleum based lubricants has also been discussed in this paper.

I. INTRODUCTION

Lubricants are being used since the invention of wheel. The main function of lubricant is toreduce the frictional force by decreasing the friction coefficient and since that age, lubrication became the basic need for every moving mechanical machine [36, 20].

In any mechanical equipment, the moving part causes a friction force because of the surface irregularities of two superficial contacting surfaces [24, 50]. Every working surface is rough and this roughness causes thousands of microscopic barriers which generates a reverse force against the movement of that surface. This reverse force is known as friction force [54]. There are basically two losses induced by friction force that is the loss of energy and the depreciation of material or wear loss which can lead up to the mechanical failure of the engine, gear, bearings or any other moving part of the machine [5, 12].

The tribological study of energy concludes that 33% of energy from fuel is wasted by friction losses of a moving machine [19]. The calculation of energy consumption of vehicles reveals that if we consider just heavy duty vehicles like buses and trucks, about 18000 million liter fuel were wasted by friction losses occurred in year 2012 globally [14, 40] which is a shocking figure.

The losses generated by friction can't be overcome but can be reduced up to an extent by the proper lubrication of the machineries. As a result of this, the enhancement of lubricating oil also becomes a big concern. [11].

Nowadays, lubricants are produced in a large scale by various methods but mostly they are being produced by petroleum based feed stocks. According to a key note paper, presented by head of global strategic marketing and chief sustainability officer at 16th ICIS world base oil & lubricants market in London, the global lube market volume was at around 31.9 million tons in the year 2009 and increased with 10% in the next year [15] that became 36.1 million tons in year 2017. It is estimated that the demand of lubricant will grow continuously by up to 2-3% per year.

The base material of almost every lubricant is petrochemicals which are obtained by crude petroleum [32, 43]. Although petroleum based lubricants have many useful characteristics yet these are non-renewableand toxic to the environment [59].

Some machines like agriculture equipments, food industries and water pumps have direct contact with food and human lifestyle need a safe and nontoxic lubrication. Petroleum based lubricants can cause dangerous contamination if used directly in these fields. Improper disposal of petroleum based lubricants can cause serious contamination in water and can vitally affect theaquatic ecosystem [1, 17, 53]. Also petroleum has limited source which is reducing day by day because of this the price of petroleum based lubricants is also increasing exponentially [38].

Major portion of petroleum lubricants end up polluting the environment. The solution of this problem is hidden behind the eco-friendly biolubricants. Biolubricants have zero toxicity to the environment because of their excellent self-degradable properties and the sources of biodegradable lubricants are themselves biodegradable in nature as they are derived by vegetable oils which are produced through renewable sources such as plants, seeds and fruits. That's why lubricant industries are replacing the petrochemical based feedstocks with vegetable oils as base material for synthesis ofbiolubricants.

Biolubricants can be manufactured by both vegetable oils and animal oils i.e. generally low cost non edible oils. Some of the vegetable oils which are being used for biolubricant production arekaranja oil, neem oil [29], palm oil [23], waste cooking oil, rapeseed oil, castor oil [41], linseed oil, mahua oil [23] and many more.

The main component of vegetable oils used for making biolubricants is triglyceride. The triglyceride is chemically modified for synthesizing the biolubricants. There are various methods of chemical modification of triglyceride like transesterification, epoxidation, synthesis of estolides, synthesis of polyolsetc[13]. These modifications enhance the physicochemical characteristics of the vegetable oil and make it suitable for lubrication.

Vegetable oils based lubricants have various advantages like high biodegradability, renewability, lubricity, higher flash points, less toxicity and their good anti-wear characteristics still like the two faces of a coin, there are also some disadvantages of biolubricants which make it unsuitable for using at a large scale i.e. their poor thermal and oxidative stability, higher pour points, lower viscosity index, etc. These drawbacks are also unavoidable as they can broadly impact the lubricant's performance.

To reduce these undesirable properties we need to add some external materials which can modify the lubricant without affecting its positive qualities. These external materials are called lubricant additives.There are hundreds of natural as well as synthetic additives which are being used to modify lubricants performance since centuries. In 1930s natural waxes were used to increase thermal stability and oxidative stability. Some polar solvents like kerosene [42] werealsoused to mix in the lubricant for reducing viscosity but these natural additives had limited advantages [45].

Nowadays, some polymeric waxes, inorganic compounds and surfactants are being used as multipurpose synthetic lubricant additives. Polymethyl methaacrylate (PMMA) is the most common polymeric lubricant additive which is being used on a large scale by almost every lubricant manufacturer.

Although these additives are somehow fulfilling our desires yet with the technological improvement, lubricant additives have also been modified more and more. The introduction of nano technology has made an evolutional change in the area of lubricant additives.

Nano lubricant additives are fine inorganic elements or compounds, stabilized by surfactants or stabilizers. The main advantage of using nano lubricant additives is its suitable size to enter the contact acuteness, excellent surface reaction and thermal stability [26].

Recent studies in the area of lubricant additives have proved that the addition of surface modified nano particles to the lubricant such as metal sulfides [10], metal oxides [6], pure metals [30], carbonates [48], borates [22], nano Carbon materials [21], organic materials [49], and rare earth metal compounds [63] has superb effectiveness to the various properties of lubricants [60].

Overall this review paper focuses on various methods of synthesis of biolubricants, their advantages and disadvantages, types of lubricant additives for improving various properties of lubricants accordingly, implementation of nano technology in the area of lubricant additives. Various methods of production of nano lubricant additives, their advantages and disadvantages along with their physicochemical effect on the lubricity of base lubricants are also discussed in the paper.

II. SYNTHESIS OF BIOLUBRICANTS AND TYPES OF LUBRICANT ADDITIVES

A. *Methods used for the synthesis of biolubricants*

Biolubricants aresynthesized by chemical modification of vegetable oil. There are number of chemical reactions which can be used formodification of triglycerides as shown in the table [3].

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Table 1: List of chemical reactions for the synthesis of biolubricants along with the catalyst used

Modification	Catalyst
Modification of Carboxyl Groups	
Esterification/transesterification	Acids, Bases
Estolides	HClO4
Modification of fatty acid chains	
Selective hydrogenation	Copper catalysts
Dimerisation/oligomerisation	Aluminosilicates
Diels-Alder cycloaddition	-
Telomerisation	H2O vapor
Co-oligomerisation	RhCl3.3H2O
- Hydroformylation (oxo-synthesis	Rh(Ph3P)3
Friedel-Crafts alkylation	Et3Al2Cl3
- Aminoalkylation	[Rh(COD)Cl]2
Friedel-Crafts acylation	EtAlCl2
Ene-reaction	EtAlCl2, SnO4 Mn(OAc)3, Cu
- Radical addition	Mn(OAc)3, Cu
Acyloxylation	Nafion/SiO2
Cyclopropanation	CH2I2, Zn(Cu), Et2Zn
Metathesis	Grubbs catalyst
Epoxidation	Peracids, chemo-enzymatic
- Ozonation	-
Oxidative cleavage	Pb3O4

Source: A review of bio-lubricant production from vegetable oils using esterification transesterification process conference paper in MATEC web of conferences march 2018

As we can see, the vegetable oil based lubricants can be made by so many different chemical reactions but among them only esterification/transesterification, epoxidation, conversion into estolides and conversion into organic polymers are the most used methods for the industrial production of lubricants.

- *Transesterification*

Production of fatty acid alkyl esters by reacting fatty acid or oil with alcohol is called transesterification. This fatty acid methyl ester can be used as biofuel or bio lubricant. The reaction can be catelyzed by both homogenious catalyst and hetrogenious catalysts [35].The most common catalyst used for industrial production of fatty acid methyl esters is sodium methoxide [16]. Generally short-chain alcohols such as methanol/ethanol are used (for biodiesel production) as a base. Low quality feedstocks, includingnon-edible vegetable oils, animal fats, waste cooking oils, and grease, contain a significant amountof free fatty acids (FFA). When FFA is high, the sodium methoxide catalyst cannot be used because ofsoap formation. Acid catalysts work much slowly than a base catalyst in a transesterificationreaction [9]. Moreover, because of the corrosive nature of acid catalysts; expensive acid-resistantreactors must be used. Therefore, in order to convert a low quality feedstock into biodiesel, first theFFA present in the feedstock should be converted into esters with an acid catalyst to obtain a mixtureof fatty acid methyl esters and triglycerides. The esters in the second step are transesterified withmethanol catalyzed by a base to obtain biodiesel. The reaction has been depicted in figure 1.

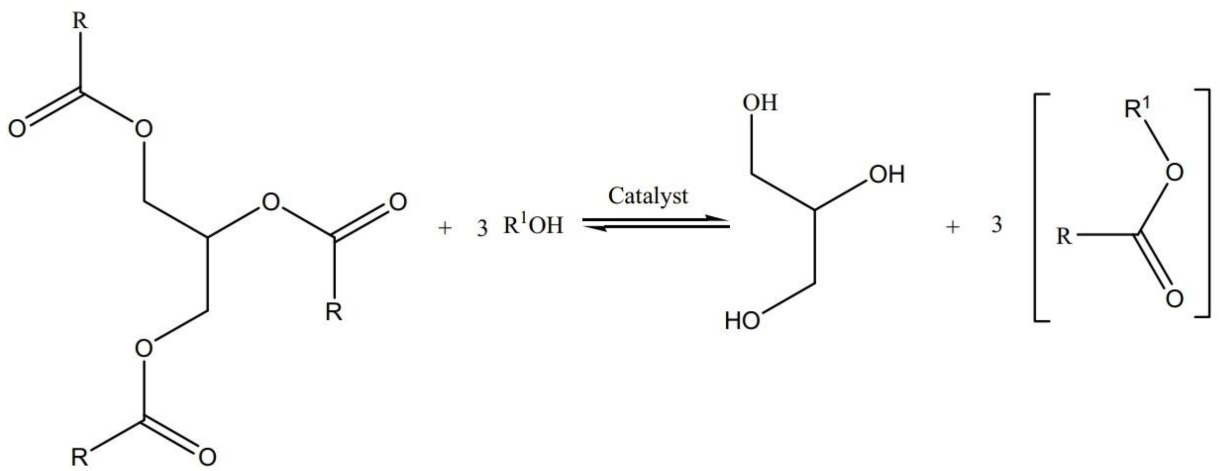

Fig. 1: Transesterification reaction of try glyceride for the production of biolubricant[49]

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➢ *Epoxidation*

Epoxides are basically cyclic ethers which contains three elements in the epoxide ring. Epoxidation is one of the most important reactions of unsaturated fatty acids for synthesizing bio lubricants. The doublebonds in the vegetable oils are used as reactive sites in various chemical reactions and they can also be functionalized by epoxidation. Therefore the presence of double bond in the fatty acids of triglyceride is mandatory for the epoxidation reaction. The utilization of epoxidizedvegetable oils has become more common in the past few years.Epoxidized oil containsepoxide groups or oxirane rings. Epoxidation reaction involves reaction of an alkene with an organic peroxy acid.Epoxidation reaction generally takes place in two steps:

- Formation of peroxy acid
- Reaction of peroxy acid with the unsaturated double bond.

The conversion of ethylenic unsaturation into epoxide depends upon various factors liketemperature,ratio of ethylenic unsaturation to percarboxylic acids, catalyst & catalyst concentration, rpm and addition time of H_2O_2. Addition of H_2O_2 is done slowly to avoid zones of high peroxide concentration which leads to formation of explosive mixtures [49]. The reactions involved in epoxidation are depicted below in figure 2.

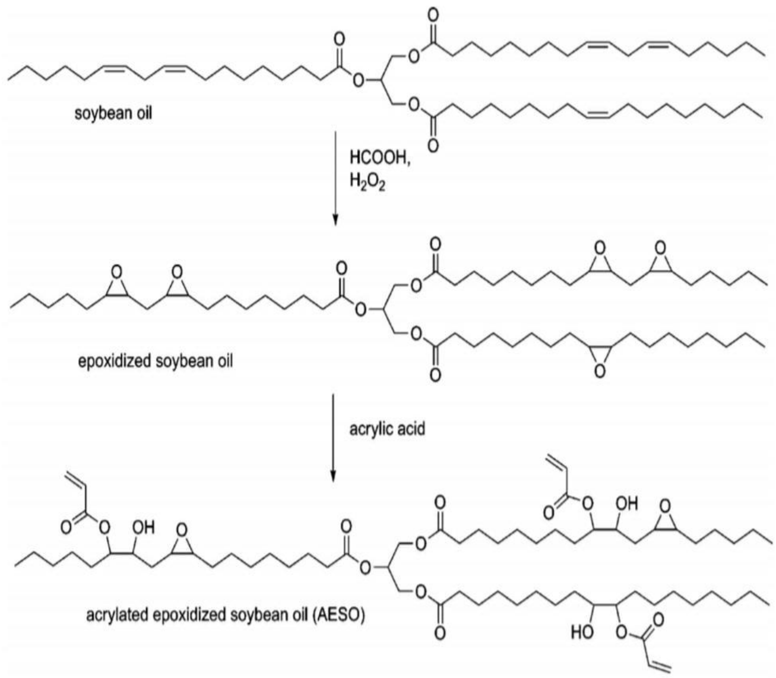

Fig. 2: Synthesis of acrylatedepoxidized soybean oil[2, 46]

➢ *Synthesis of Estolides*

Estolides are also basically esters which are obtained by reaction of both carboxylic group and C=C double bond of a fatty acid molecule.Estolides can be synthesed by both oleic acid and ricinoleic acid by using different acid-catalystsas shown in the figure 3. ArukaliSammaiah et al, 2016 studied the synthesis of estolidesfrom castor oil and methanol using H_2SO_4 as catalyst. These esters have excellent cold temperature properties and oxidative stability. Thus they are used in many industrial applications. Estolides can be used as bio lubricants as well as lubricant additives as pour point depressant. It can be used with different ranges of viscosity depending on their chemical structure,degree of polymerization etc [49].

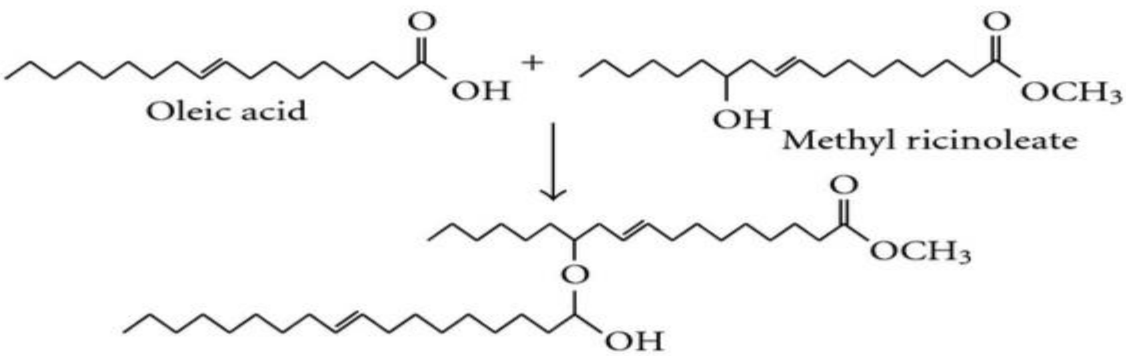

Fig. 3: Synthesis of esteloids by oleic acid and methyl ricinoleate

➢ *Synthesis of organic copolymers*

Biolubricants can also be synthesized by homopolymerization or copolymerization of vegetable oils or fatty esters or their epoxy derivatives with suitable co-monomers. There are various methods of homopolymerization and copolymerization of vegetable oils and their epoxy derivatives for example cationicpolymerization, free radicalpolymerization, ring openingpolymerization, andcondensation polymerization. Thermally polymerized soybean oil mixed with suitable additiveswas used as bio-based gear oil. Bio-based polyesters show the extreme pressure additive qualities in mineral oil [59]. Polymerization based lubricants show excellent thermal and oxidative stability. Polymerization of vegetable oils and their derivatives in the presence of different organic or inorganicnano-fillers produces polymer nano-composites, which are extensively applied in the automotiveindustry, especially as an anti-wear coating/additive in lubricants [8].

The chemical reactions for the synthesis of polymerized soybean oil are shown below in figure 4.

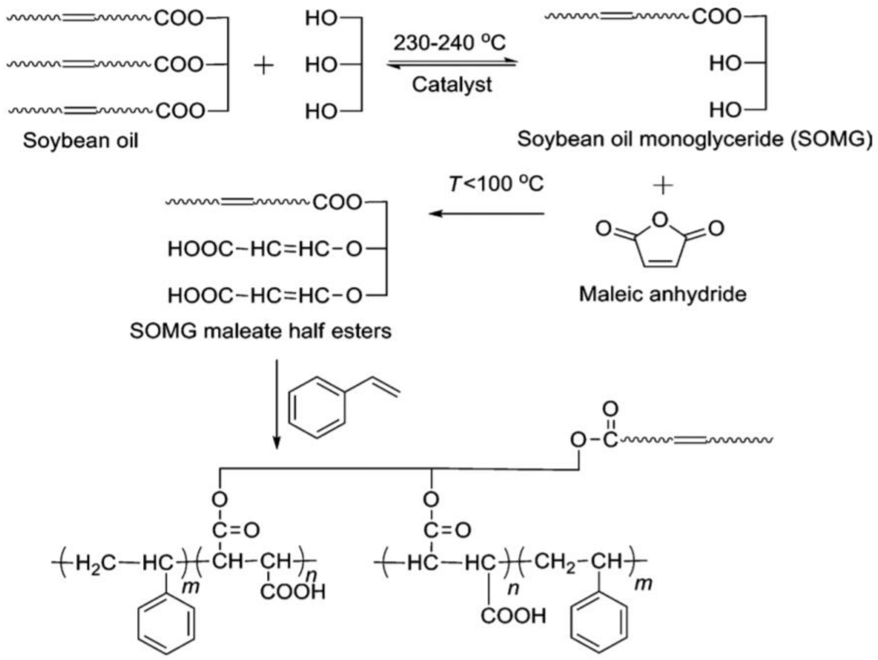

Fig. 4: Synthesis and polymerization of soybean oil mono glyceride maleates [8]

B. Lubricant additives

Additives for the lubricants may be both organic and inorganic compounds in nature which are suspended in the base lubricant to enhance its performance. They typically range between 0.1 to 30 percent of the lubricant oil volume, depending on the requirements. The basic purpose of a lubricant additive is to;

- Improve theproperties of lubricantswith the addition of antioxidants, anti-foam agents, corrosion inhibitors and demulsifying agents.
- Impart new properties to the lubricantwith extreme pressure additives, detergents, metal deactivators and tackiness agents [31].
- Reduce the undesirable properties of lubricantswith pour-point depressants and viscosity index modifiers.

On the basis of performance of base lubricant and the effect on physicochemical properties, the lubricant additives can be classified as:

➢ *Pour Point Depressants*

The performance of a lubricant to flow under low-temperature and low-shear conditions is crucial for lubricity. If the equipment runs below pour point, the lubricant leads to its worst condition and becomes solid which causes the equipment failure.Earlier in 19s, this problem was being reduced by adding any solvent like kerosene but it affectsthe viscosity also. There were some other alternatives like addition of microcrystalline paraffin waxes asphaltenic resins etc. Unfortunately these materials were effective but not broadly applicable. Nowadays, the polyalkylmethacrylates are worldwide used pour point depressant they are synthesised by the mono polymerization of vegetable oils with alkylmethaacrylate. The most common example of polyalkylmethacrylates is polymethylmethaacrylate(PMMA).These are nothing but only synthetic waxes which gives the better results than natural waxes[47].

➢ *Viscosity Index Improvers*

The most important characteristic of a lubricant is its viscosity. It is the measureof inner friction which works as a resistance to the change of molecular positions influid flow when they are under the impact of shear force. In other words, it is theresistance of fluid particles to shear.The viscosity index improvers impact the oil behaviour as far as flow characteristicsare concerned. The main characteristics of viscosity index improversare:

- Maintaining the oil in liquid form at lower temperature.
- At higher temperatures they provide higher viscosity to oil which helps in providing a necessary oil film thickness and small oil consumption.

There are basically 3 most known V I Improvers i.e.

- polymethacrylates (PMA),
- olefin copolymers (OCP),
- Hydrogenated styrene-diene copolymers.

➢ *Antioxidants*

Oxidation is one of the major problems for biolubricants which occurs because of the open exposure of lubricant to air and catalyzed by metal ions.

Antioxidants are defined as the chemicals which can reduce the rate of oxidation upto a desirable extent. According to the mechanism of action, antioxidants are classified into 3 parts;

- Primary antioxidants (radical scavengers)
- Secondary antioxidants (Peroxide decomposers)
- Metal deactivators (complex-forming or chelating agents) [37].

The most used antioxidants for lubricants are: tocopherols, propyl gallate (PG), ascorbylpalmitate (AP), and some synthetic antioxidants butylatedhydroxy anisole (BHA), butylatedhydroxy toluene (BHT), mono tert-butyl hydroquinone (TBHQ), or 4,40-methylenebis(2,6-di-tert-butylphenol) (MBP)) which have been used for improving their resistivity towards oxidative agents.
In recent researches, several cellulose fatty esters have also been developed as the lubricant additive, and are modified to cellulose ferulate, cellulose lipoate and α-tocopherulatemainly forantioxidant applications[37].

➢ *Anti-Foaming agents*

Foams are thermodynamically unstable dispersions of a gas in a liquid [7]. Formation of foam causes more interaction of air with lubricant which increases the rate of oxidation. Besides this, the formation of foam causes the excessive wear in machine parts, less lubrication, poor heat removal, and overallhigh energy losses. Thus antifoaming agents become the critical part of the lubricants. Silicones are considered as the best antifoaming agents but they have limited use in lubrication. Some other polymeric hydrocarbons like polyacrylates, polypropylene glycols (PPGs) and EO/PO copolymers are also effective foam control agents because of their low foam characteristics and inverse water solubility. These products are available in liquid form, with different molecular weights and viscosities to meet diverse needs [7].

➢ *Metal Deactivators*

Metal deactivators are chelating agents which inhibits or reduces the metal ions produced by oxidation or undesired acidic or basic action on the metal surface.

The metal ions catalyses the rate of oxidation and causes the formation of metallic bases which reduces the performance of lubricant and its self life.The most used metal deactivators are;Salpn ligand (N,N′-bis(salicylidene)-1,2-propanediamine) and EDTA (Ethylenediaminetetraacetic acid)[62].

➢ *Anti-Wear Agents*

Anti wear agents inhibits the performance of a lubricant by preventing the metal to metal contact of any equipment. They form a thin layer between two metal surfaces by chemical deposition or adsorption. Thus these additives do not only work as an anti wear agent but also reduces the friction upto an ambient pressure. Although we have to use some extremes pressure additives for dealing with high pressure but for low pressures, theanti-wear agents are enough for reduction in friction.

The common Anti wear agents used as lubricant additives are; sulfurized vegetable oils, tritolyl/-phosphate, chlorinated paraffins, alkyl-and aryldi- and tri-sulfides, triphenylphosphorothionate [62].

➢ *Corrosion & Rust Inhibitors*

Corrosion inhibitors are the compounds which reduces the corrosion of metals like copper aluminums zinc etc whereas Rust inhibitors prevent the corrosion of iron by making a protective film or by adsorbing on its surface. These additives are used in traces.The anticorrosion additive concentration equals about 0.1-2%[4]. Table 2 shows the various types of corrosion inhibitors along with their uses and examples.

Table 2: Types of corrosion inhibitor their uses and examples [4]

Corrosion inhibitor	**Uses**	**Example**
Sulfur-containing corrosion additives	To prevent corrosion of lead-copper bearings, sulfuratedterpines	Di-(3,3,5-trimethylhexyl), sebacateDi(2-ethylhexyl)- sebaeate
Nitrogen-containing corrosion additives	To prevent corrosion of light metals,	Benzotriazole,benzimidazole, imidazole, 1,2,3-triazole,2-methylbenzimidazole, 3,5-dimethyltriazole, or 3,5-dimethylbenzotriazole
Sulfur, nitrogen and phosphorous-containing corrosion additives	For esters and mineral oils	Tri(alkylamido)-thiophosphates
Boron -containing corrosion additives	To prevent corrosion of copper-lead alloys	P-xylylenediamine and glycol-boric acids
Other corrosion inhibitors	To prevent corrosion of bearings	Phthalic acids and ternary amines or hydroxylalkyl amines

➢ *Detergents*

Detergents work in two ways. Theyneutralize the acid produced on the surface of metal as well as they suspend the impurities by suspending it inside. Thus detergents do not only keep the metal surface clean at high temperature but also prevents the corrosion by neutralizing the acids.

Detergents used as lubricant additives are generally anionic surfactants which provide the reverse alkalinity to the base lubricant. Generally higher molecular Calcium, Magnesium, Barium or Sodium based surfactants are used as detergent additives. These surfactants works as a cleansing agent also by trapping the impurities (dirt, water, fuel, process material, and lube degradation products such as sludge, varnish, oxidation products) by forming the micelle and trapping the impurities inside in a suspended form as shown in figure 5 [18].

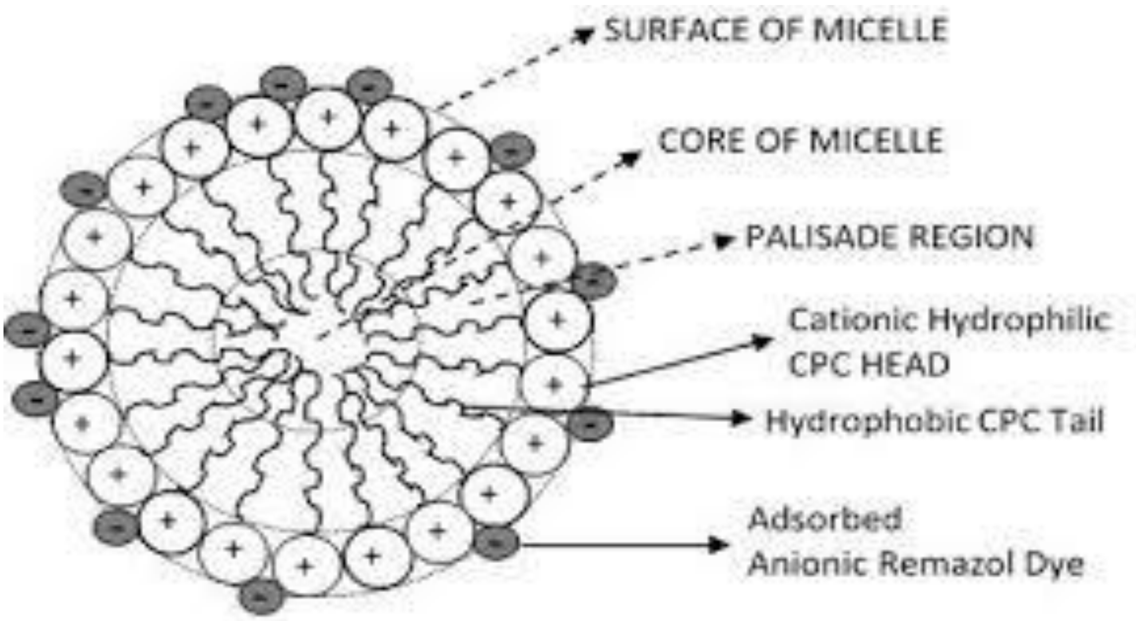

Fig. 5: Micelle structure: Structural Biochemistry/Lipids/Micelles technologies.

➢ *Dispersants*

Dispersants are used to keep the base lubricant free from contaminants. It suspends the impurities and does not allow it to agglomerate. Theyare used as a mixture of detergents and dispersants. The mixture of detergent with dispersant are more suitable for neutralizing the acidic contaminants and provides better dispersion of impurities.

Dispersants form a protective film on the surface of metal which prevents the contact of metal to air which reduces the rate of oxidation and deposition of sludge and dirt like impurities[18].

The common dispersants used as lubricant additive are Polymeric alkylthiophosphonates and alkylsuccinimides, organic complexes containing nitrogen compounds.

➢ *Friction modifier*

Friction modifiers are the oldest additives used for lubricating oils as they fulfill the most desirable requirement of lubricants that is reduction of friction between two metal surfaces.

The long chain fatty acids were the well used friction modification in 1990s.Earlier it was observed that organic surfactants have also more friction reducing capacity than free fatty acids. They work by forming a thin layer between two metal surfaces and prevent the direct metal to contact.The main challenge for a friction modifier is that it must work properly at different physical conditions. They should retain their effectiveness in a range of temperature and pressure[81].

The common friction modifiers used as lubricant additives are; Organic fatty acids and amines, lard oil, high molecular weight organic phosphorus and phosphoric acid esters etc [18].

C. Nano-Lubricant Additives

There are large numbers of lubricant additives used for fulfilling the different types of requirements. Some specific additives are being used for fulfilling a desired purpose and also there are some multipurpose additives which fulfillmore than one requirement at the same time. For example, Silicones arejust used for fulfilling anti foaming characteristic; there is no other application of silicones, but on the other hand poly methyl acrylates, act as a viscosity index improvers, friction modifiers, pour point depressants and also enhance thermal stability simultaneously. The recent research in lubricant additives shows that the nano based lubricants have significant impact on the performance of lubricants. These additives have superior performance than conventional polymer based additives. [33].

L.K. Hudson et al, 2006 studied the preparation of nano based lubricant additives byoverbasing process. The mechanism of overbasing is based on macro emulsification process. The reaction system consist an excess of nano sized inorganic base material, a suitable surfactant, and an appropriate polar solvent like mixture of water and alcohol.

The reaction causes the formation of micelle which includes the inorganic base material trapped inside the micelle and the outer layeris formed by some sort of surfactant.Thismethod is also called theOxide/Hydroxide processwhen the base material is taken as an inorganic metal hydroxide[33].

➢ *Structure of nano-Lubricant Additive*

The nano based lubricant additive has a micelle like structure in which the fine nano sized inorganic base particles are trapped into a surface active agent like any surfactant or soap. Thus the structure of a nano lubricant additive can be categorized into two parts as shown in figure 6.

- The outer part of the micelle i.e. any surfactant or soap
- The inner part of the micelle i.e. any sort of inorganic base[56].

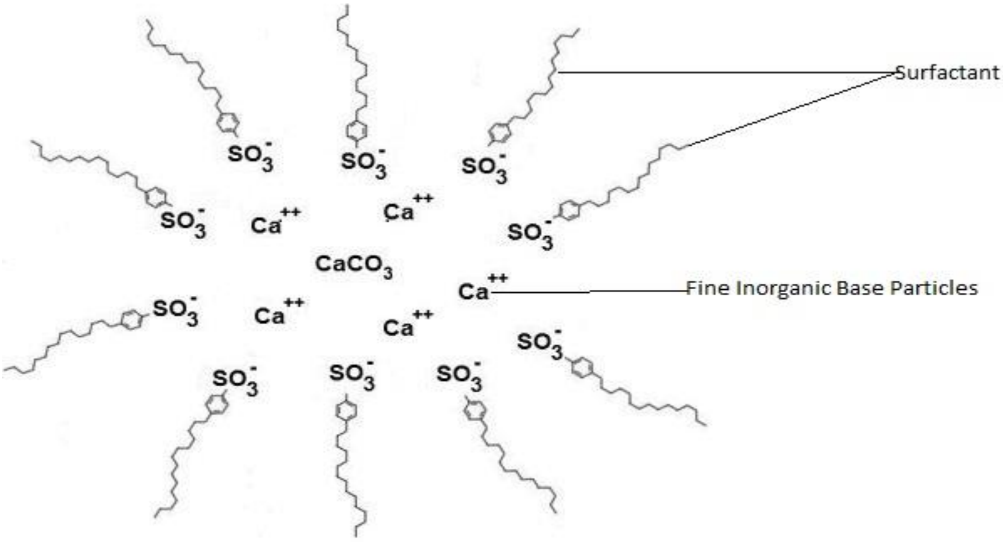

Fig. 6: Structure of nano lubricant: Diesel Engine Lubricants, HannuJääskeläinen, W. AddyMajewski

➢ *Selection of surfactant*

The surfactants form the outer layer of the micelle of nano based lubricant additives. Thus it plays the most important part in the efficacy of additive. There are hundreds of surfactants used for nano lubricant additive manufacturing such assalicylates, silicates, sulphonates, carboxylates, phosphinates, alkylphenates, sulfurized alkyl phenates,sulfurized phosphonatesetc according to their performance and requirements. Sometimes the mixture of more than one surfactant is used to form more efficient lubricant additives. The desirable concentration of surfactant mixture can be calculatedhydrophile-lipophile balance (HLB). Ruijin Wang et al, 2018 analyzedthe respective properties of several surfactants which are tabulated below [51]:

Table 3: Properties of surfactants as stabilizers for nano lubricant additives

Deterrgents	Approx, TBN range	Hydrolytic stability	Oxidation stability	Thermal stability	Detergency	Rust inhibition	Antioxidant
Phenates	0-300	Good	Very good	Excellent	Good	Low	Very good
Sulphonates	0-500	Moderate	Poor	Excellent	Good	Good	None
Salicylates	0-300	Good	Very good	Excellent	Good	Low	Very good
Phosphonate	0-80	Moderate	Good	Moderate	Excellent	Good	good

➢ *Selection of Inorganic base material*

The inorganic base material is the second most important part of a nano based lubricant additive as it acquires the inner core of the micelle. It may be any kind of inorganic base or metal of nano size. But according to cost and performance, the most commonly used core materials are calcium, magnesium, sodium, zinc, boron, nikil, carbon and their basic hydroxides, salts and alloys. Sometimes the mixture of more than one material is used as a nano base material [20]. Among these, the $Ca(OH)_2$ is one of the most used base material as core which is carbonized with CO_2 at high temperature and pressure before overbasing[51].

According to the chemical composition, inorganic base material of a nano lubricant can be categorized as:

➢ *Metal Nano -Particles as base material*

Nano metal particles are high surface active powdered materials. They are being used as catalysts, semiconductors, magnetic and photonic field since long ago. They show the excellent tribological effectiveness and self-repairing properties as well. Because of high surface activity, they shows very less effect on the efficacy of base oil but their performance can be modified by surface modification techniques or overbasing[44]. Overbasednano metal based lubricant additives show a tremendous effect.There is a number of metal based nano lubricant additives used as per requirements:

Padgurskas J. et al, 2013 analyzed nano copper based lubricant additives which are commonly used as diesel engine lubricants. It shows the excellent friction wear and self-repairing properties.Iron and Tin based nano additives are used in space industries for lubrication and anti-wear properties [44].

- *Metal oxide and hydroxide as base material*

Metal oxides and hydroxides are relatively cheaper than pure metals because of the ease of conversion of metal oxides and hydroxides into nano size. The most common metal hydroxide is $Ca(OH)_2$ which is carbonated with CO_2 at high pressure and then overbased with any surfactant. Besides it, some other oxides as TiO_2, ZnO, $ZnAlO_3$ etc has also shown a positive effect on lubricant performance Wu Y.Y. et al, 2007analyzed TiO2 and also CuO behaviors as nano lubricant additives. It was shown that the addition of two different nanoparticles to oil decreases its friction (CuO performed shown better results than TiO2 [59].

Silva J. D. et al, 2006 found that ZnO has a very high anti corrosive and anti-wearbehavior and increases the oxidative stability. $ZnAlO_3$ also has a tremendous dispersive ability and thermal as well as mechanical stability. It is being used in aerospace industries as catalyst, ceramic and anti-thermal coatings [53].

Recent research shows that the mixture of more than one oxide and hydroxides has enormous effect on dispersive properties [57].

- *Boron compound Nano particles as base material*

The use of Boron compounds as base material is yet a matter of researchstill a lot of research has been done in the field of Boron compound based lubricant additives. Zaho G. et al, 2014 studied that the nano Calcium borate synthesized by ethanol supercritical fluid drying shows the wonderful load carrying and anti-wearing capacity when used with lithium grease. The nano Zinc Borate shows a good anti wear and friction reducing properties with sunflower oil base material. This is also a best alternative of ZDDP for engine oil lubrication [64]

- *Nano carbon particles as base material*

The scope of nano carbon ismagical in lubricating industries. There are basically three isotopes of carbon which are generally used as nano materials i.e. Graphite, Fullerene, and Diamond. The friction and friction coefficient can be controlled by Graphite and Fullerene isotopes. Graphite nano particles are used as solid lubricants also in cutting tools [52].

Nano carbon particles are classified into four parts i.e. zero dimensional nano carbon, one dimensionalnano carbon, two dimensional nano carbon and three dimensional nano carbon.

The use of different types ofnano carbon is tabulated below in table 2.

Table 4: Types of nano carbon along with their example and uses:

Nano-Carbon	Example	Uses
Zero dimensional	Fullerene	Friction modification, Adsopbtion
One dimensional	Carbon nanotubes	Wear and Friction Behaviour
Two dimensional	Graphene	Anti wear and Friction modification
Three dimensional	Graphite, Diamond	Ball bearing, solid lubrication

D. Method of synthesis of Nano-Lubricant additives through Overbasing

The process of manufacturing is based on the Nano emulsification or ultrafine emulsification where the colloidal solution of nano particles is formed with the help of suitable surfactant or mixture of surfactants [39]. The methods of nano emulsification can be classified as:

- *Two step method*

This is the most widely used method for preparation of nano emulsions. In this method, the inorganic base material is dried and converted into nano particles in the first step and then this powder is dispersed into a solvent with the help of ultra sonic mixing, magnetic force agitation, high shear mixing and ball milling in step two.This suspension has a very high tendency of coagulation as the nano particles are highly surface active materials. Thus we need to stabilize this suspension with a mixture of surfactant [61]. Two-step method is one of the most economic methods to produce nanofluids on industrial scale, because nanopowder synthesis techniques have already been scaled up to large scale production.

Due to the difficulty in preparing stable nanofluids by two-step method, several advanced techniques are developed to produce nanofluids, including one-step method.

- *Single step method*

Single step method for production of nano emulsion involves different types of chemical reactions to convert the core material into suspended form. And the suspension is then stabilized by surfactants. This process does not require drying or milling or high shear mixing as the suspension process is done with chemical reactions. And the suspension, formed by this process is a homogenous colloidal solution. The chance of coagulation of emulsion is also less than two step process. But the main drawback is that this process needs a specific chemical reaction and physical conditions for the formation of a particular colloidal solution. That is why this process can’t be applied for industrial scale production. The process is generally used for research purposes [27]

- *Other methods*

There is some advance research related to nano emulsion formation as; Ethanol Supercritical fluid drying for production of Calcium borate [24],Phase-transfer method is also used to obtain monodisperse noble metal colloidsand kerosenebasedFe3O4 nanofluids [62], Chemisorption of fluid can also be used for kerosenebasedFe3O4 nanofluids [34].

III. ENHANCING THE STABILITY OF NANO EMULSIONS

The stability of emulsion is acquired by add the detergent. The process of stabilization is very simple as we directly add the required amount of surfactant with a medium agitation. The amount of surfactant required can be calculated by HLB method. The surfactant contains a hydrophobic carbon chain and a hydrophilic group which causes the formation of micelle and traps the inorganic base inside. The types of surfactants have been discussed before [57]

IV. ADVANTAGES OF NANO LUBRICANT ADDITIVES OVER CONVENTIONAL ADDITIVES

The performance of a nano lubricant additive depends on their base material and the surfactant used for surface modification of that base material. In short we can say that every nano lubricant additive have their own specifications, But the one thing, which is common in all types nano additives is its smaller particle size and this is the most special thing of it. Lubrication is a surface phenomenon and the smaller particle size makes a lubricant additive more likely to show its performance [55, 57,59,64].

V. CONCLUSION

A huge amount of pollution caused by toxic petroleum based lubricants can be controlled by replacing them with vegetable oil based lubricants. But the limitations of biolubricants over petroleum based lubricants are their thermal stability, oxidative stability and viscosity index.These limitations can be overcome by adding some lubricant additives. There are many additives which are currently used by lubricant manufacturers according to requirements and their performance. However more improvements are required and can be done with the help of nano technology in the area of lubricant additives.

Introduction of nano technology has shown enormous advantages in the field of lubricant additives because of their high reactivity, excellent biodegradability and zero toxicity. Although the technology of manufacturing of nano lubricant is expensive yet it can be adopted as they are used in traces as compared conventional additives.

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