

GENERAL INTRODUCTION

A lubricant is a substance that is incorporated in an engine to reduce friction and to ease constant movement between metal surfaces in contact[1], thus reducing heat generated on prolonging friction. This property of minimizing friction by a lubricant is known as lubricity. The history of the use of lubricants is thousands of years[2]. During the time of the pyramids, building stones were slid on oil-impregnated lumber. In ancient civilization, soaps were used to reduce friction in wheels. Lubricants based on plant oils and animal fats were used in the Roman era. But with the invention of vacuum distillation of petroleum in the early 1900s, the focus shifted toward petroleum-based materials[3]. Again, with the demanding complexities of modern engines, the demands placed upon the lubricant also became increasing.

To assist the relative motion and to prevent damages, lubricants in form of solid, liquid, or gases are intruded between two surfaces. A gaseous film is usually favored for low contact stress while liquid films are widely used in a most modern engine to perform lubrication over a while. The solid films are usually practical for contacts with low sliding speed[4-5]. The chief ingredient of lubricating oil is the base oil and depending upon nature[4-5], it might be classified as mineral base lube oil, synthetic-based lube oil, or as a lube oil of bio origin.

- **BASE LUBE**

The most commonly used commercial lube oil around the globe is the mineral-based lube and is derived directly or indirectly from refining petroleum. Base oil is extracted as a heavier part of the refining process of crude oil. It is composed of a complex mixture of hydrocarbons and generally includes aromatic, olefinic, paraffinic (linear/branch), and naphthenic hydrocarbons, molecular weights ranging from C₂₀-C₇₀[6]. The synthetic lube oil generally includes poly alpha-olefins,

synthetic esters, silicones, etc., Bio-based lube derived from plants and animal sources.

The lubricating oil provides a fluid layer impregnated between moving metal surfaces and thus, reduces friction and the heat generated by the engines. It also has a huge number of different purposes like increasing liquidity at low temperature reducing temperature variation of viscosity i.e modifying Viscosity Index, wears prevention, inhibiting the formation of rust, protecting the engines against corrosion, etc[7-8].

- **ADDITIVES**

Engine lubricating oil makes up nearly one-half of the world's lubricant market but unfortunately, they do not meet all the requirements of modern engines. Engine oil is, therefore, formulated with a mixture of base oil and a specifically manufactured additive for certain operating conditions. **Additives** are materials that are specifically devised for enhancement of the physical and chemical properties of the base oils, which as a consequence results in enhancing the equipment life and boosting the lubricant performance[9-14]. Devoid of any additives, even the best base oils cannot satisfy all types of industrial requirements. The type and quantity of additives are chosen largely depend upon the lubricant in which it is going to be used (gear oils, hydraulic oils, engine oils, etc.) and on the actual operating environments (materials, loads, temperature, etc.).

Lubricant performance depends collectively on the base oil, the additive used, and its formulation. Usually, only one type of base stock serves the purpose of a particular lubricant but sometimes mixtures of base oils are also used together, doping with a variety of additives. Besides, no single additive can satisfy the desirable performance necessary for the efficient working of an engine. Thus, several

additives are required to satisfy the original equipment manufacturer (OEM) needs and also the consumer needs. Additives are used at different concentrations ranging from 0.05 % to more than 10% by weight of the lubricant. The proportion of additives may even reach 30%[15]. It is obvious that A lubricant without the proper additive is bound to get contaminated by subsequent degradation products of the base oil and, therefore, more frequent systematic oil changes are required.

- **CLASSIFICATION OF ADDITIVES**

At present Lubricants are essential and practically all types of lubricating oil contain at least one additive, and some may even contain additives of several different types to meet different needs. Although some are multifunctional i.e. they satisfy more than one function, the more commonly used additives are discussed in the following sections in terms of their primary functions.

- **METAL SURFACE PROTECTOR**

They are also known as film-forming agents. This type of additives includes extreme pressure(EP) additives[11-12], anti-wear(AW)[16-17], rust, and corrosion inhibitors[18]or friction modifier(FM). These additives protect the metal surface by making a protective film also called tribo film through adsorption or chemical reaction and thereby inhibit the formation of rust and control wear during prolonged friction in the engine. The three kinds of additives(FM, AW, EP) are collectively called Tribo-Improvers. Detergent and dispersant additives are also considered in this group. Detergents keep surfaces free from deposits and dispersants keep insoluble soot particles suspended by micelles formation with the oleophilic and oleophobic part in their molecular composition thereby protecting the metal film free from any deposits.

- **PERFORMANCE-MODIFIERS**

These additives improve the performances of the lubricants and include viscosity index improver (VII)[6-19], pour point depressants(PPD)[20-21], Additives with high viscosity index keep viscosity change at marginal over a wide temperature range. Lube doped with high PPD inhibits wax crystal formation at lower temperatures hence modifying the attribute of low-temperature flowability in lube oil.VII and PPD additives are also called Rheo Improvers

- **LUBE PROTECTOR**

Out of the many causes of engine malfunction, the major cause is poor lubricant quality arising out of lubricant contamination, deposit formation, oil thickening, ring sticking, etc. The additives which are used to control these actions are known as lubricant protective additives. These additives protect the lubricant instead of the machinery equipment. These types of additives include antioxidants[22], anti-foaming agents[23], Antioxidants terminate the pathways of initiation or propagation or both by quenching free radicals or active molecules. The radical is produced due to thermal or shear stress or due to metal-ligand interaction in the interface. Additives of different kinds and their function are summarised in the following Table 1.

METAL SURFACE PROTECTOR			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Anti-Wear Agent	Reduce friction and wear, and prevent scoring and seizure	Zinc dithio phosphates, organic phosphates, and acid phosphates; organic sulfur and chlorine compounds; sulfurized fats, sulfides, and disulfides	Chemical reaction with the metal surface to form a film with lower shear strength than the metal, thereby preventing metal-to-metal contact
Corrosion & Rust Inhibitor	Prevent corrosion and rusting of metal parts in contact with the lubricant	Zinc dithio phosphates, metal phenolates, basic metal sulfonates, fatty acids, and amines	Preferential adsorption of polar constituent on the metal surface to provide a protective film and/or neutralization of corrosive acids
Detergent	Keep surfaces free of deposits and neutralize corrosive acids	Metallo-organic compounds of barium, calcium, and magnesium phenolates, phosphates, and sulfonates	Chemical reaction with sludge and varnish precursors to neutralize them and keep them soluble
Dispersant	Keep insoluble soot dispersed in the lubricant	Polymeric alkyl thio phosphonates and alkyl succinimides, organic complexes containing nitrogen compounds	Contaminants are bonded by polar attraction to dispersant molecules, prevented from agglomerating, and kept in suspension due to the solubility of dispersant

PERFORMANCE MODIFIER			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Pour Point Depressant	Enable lubricant to flow at low temperatures	Alkylated naphthalene and phenolic polymers, polymethacrylates	Modify wax crystal formation to reduce interlocking wax network
Viscosity Improver	Reduce the rate of viscosity change with temperature	Polymers and copolymers of methacrylates, butadiene olefins, and alkylated styrenes	Polymers expand with increasing temperature to counteract oil thickening

LUBE PROTECTOR			
ADDITIVE TYPE	PURPOSE	TYPICAL COMPOUNDS	FUNCTIONS
Anti-Foaming	Prevent lubricant from forming a persistent foam	Silicone polymers and organic copolymers	Reduce surface tension to speed collapse of the foam
Anti-Oxidant	Retard oxidative decomposition	Zinc dithiophosphates, hindered phenols, aromatic amines, sulfurized phenols	Decompose peroxides and terminate free-radical reactions
Metal Deactivator	Reduce the catalytic effect of metals on oxidation rate	Organic complexes containing nitrogen or sulfur, amines, sulfides, and phosphites	Form inactive film on metal surfaces by complexing with metallic ions

Table 1: Lube oil additive of different types

The present study includes the synthesis of some polymeric additives (acrylate, vegetable oil-based) and evaluation of their performance in the base oil as pour point depressant and viscosity index improver, in addition, to synthesize modified vegetable oils and their performance evaluation as stated above so that to identify their potential that they can be used as potential lube base stock. A brief background of these types of additives is described below.

- **POUR POINT DEPRESSANT**

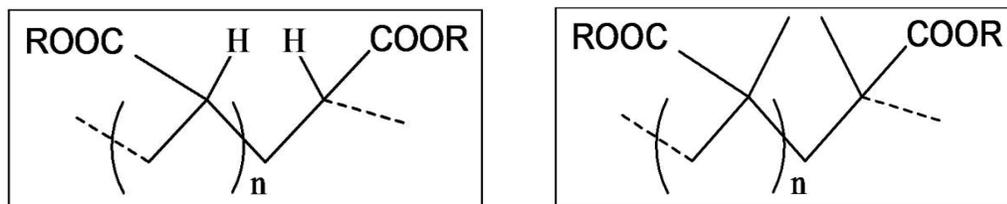
The low-temperature properties are an important part of any lubricating system. The natural paraffinic mineral base oils are always associated with some waxy materials (linear high molecular weight hydrocarbon). At higher temperatures, all the high molecular weight paraffin's remain in a dissolved state in the base oil. But, with decreasing temperature of the oil, some of these waxy hydrocarbons tend to separate as tiny crystals entrapping a substantial amount of oil, and thus inhibit the oil flow. The oil at this point (temperature) appears hazy to the naked eye and this particular temperature is defined as a cloud point. At the cloud point (i.e. the crystallization point), the oil no longer remains a Newtonian fluid but becomes a two-phase system. With a further decrease of temperature, more and more wax precipitates as crystals, and when a sufficiently large number of crystals appears, they develop into plates. The plates finally grow together to form a three-dimensional network structure and immobilize the oil. This process of the formation of a grease-like matrix is referred to as gelation and the lowest temperature at which the oil loses its flowability is termed as the pour point (PP) of the oil[24-25].

The higher the wax content in the oil, the greater the flow problems are. Generally, the pour point is proportional to the amount of wax present in the oil and a high pour point means high paraffin content in the oil. During the refining process,

most of the wax present in the crude oil is removed to obtain the base oil but some wax is still desirable for achieving the proper viscosity. The complete removal of paraffinic wax from lube oil is expensive and is very difficult. Extensive dewaxing of the base oil also increases the formation of carbon deposits and decreases the oxidation stability of base oils.

A variety of solutions are suggested to overcome these problems associated with the base oils. Preheating of the oil to modify the wax crystal structure, application of ultrasound and microwave irradiation, application of magnetic field, the addition of the light distillate to the oil are some of the techniques applied to control the low-temperature properties of the oil, but each one has its drawback and hence is not broadly accepted [26-27] Therefore, some specialty chemicals are added to the base oil to make them function efficiently at low temperatures and these are known as pour point depressants (PPD) or otherwise known as cold flow improvers (CFI), wax crystal modifiers, and paraffin inhibitors[28-30]. This CFI provides an economical way of facilitating the flow property of oil at low temperatures without compromising the viscosity benefits of the wax at higher temperatures.

Polyalkyl acrylates and methacrylates[31-32] fumarate copolymers[33], ethylene-vinyl acetate copolymers[34], alkyl esters of styrene-maleic anhydride copolymers[35], and few recently used vegetable oil polymers are some of the important additives used as PPD in lubricants[36].



Polyalkyl acrylate

Polyalkyl methacrylate

Figure 1: Structure of some commonly used pour point depressants

The mechanism of action of PPDs has been a matter of much discussion. Early indications were that the alkyl aromatic compounds form a coating over the surface of the wax crystals through surface adsorption preventing their further growth and thus their capacity to adsorb oil and form gels. Although the exact mode of operation of PPDs is not clear, it is believed that they all alter the crystal morphology by various means involving adsorption, nucleation, or co-crystallization[37-38].

As shown by Light microscopy results, wax crystals formed are generally in the shape of thin plates or blades. The PPD compounds, which generally have long hydrocarbon chains, are similar to the wax structure and, therefore, undergo co-crystallization with the wax developed in the base oil. The other polar part (in the form of acrylate, methacrylate, acetate, etc) present in the PPD molecule inhibits the lateral crystal growth by coming between the wax crystals and keeping them apart from each other thereby limiting their degree of co-crystallization[39-41]. The wax crystals are, therefore, no longer able to congeal and solidify to form three-dimensional structures and inhibit the flow of the oil at low temperatures. The PPDs do not entirely prevent the wax crystal growth, but rather lowers the temperature at which the rigid crystal structure is formed.



Figure 2: Photomicrograph images of pure lube oil (SN150) at -6°C, & lube oil + 4% (w/w) of DDMA homo polymer at -11.5 °C[58]

Although the PP of most oils is related to the crystallization of wax, the oils which are essentially wax-free, have viscosity-limited PP dependence. As the temperature is lowered in such oils, their viscosity becomes progressively higher and finally reaches a point at some temperature where no flow can be observed. Since PPDs act by interfering with the growth and interlocking of the wax crystal structure, the PP of such oils cannot be altered with PPDs.

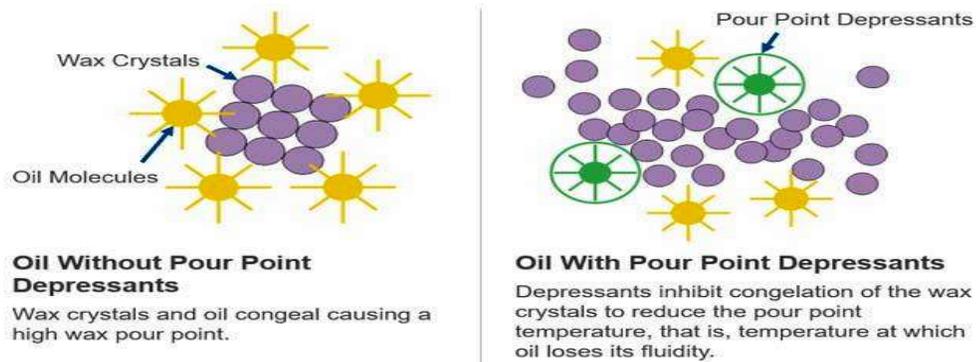


Figure 3: Schematic representation of the action mechanism of additives on wax crystals

Lubricating oils without PPDs can have a serious negative impact on engine performance. The extra workload on the engine, to overcome the increased viscosity due to wax formation, can cause cold start-up problems and decrease its lifetime. PPDs are, hence, used in all types of lubricants including crankcase engine oils, hydraulic fluids, automotive gear oils, etc.

- **VISCOSITY MODIFIER**

The viscosity of a fluid is the measure of its resistance to steady deformation by tensile stress or shear stress or its resistance to flow. For liquids, it generally refers to the informal concept of thickness. The viscosity of an oil is significant for its cooling and lubricant properties. The effectiveness of lubricating oil in minimizing friction and wear is to a great extent influenced by its viscosity. For oil of high

viscosity, the solid surfaces in contact are fully separated by a thin film of the oil. This condition is known as hydrodynamic lubrication. For low viscous oil, the hydrodynamic pressure generated is insufficient to fully separate the surfaces and, therefore, the two opposing surfaces come into contact with each other. This condition is known as boundary lubrication. The optimum viscosity required for any lubricated system depends on the load to be supported and also on the relative velocities of the surfaces.

If the hydrodynamic lubricant film becomes too thicker, a large amount of energy is wasted in shearing the film and the heat so generated accelerates the unwanted decomposition of the lubricant. In the boundary lubrication condition, a large amount of energy is wasted in overcoming the frictional forces. Also, the wear of the machines arising from friction reduces the equipment's life span. Since different machines differ in loads and velocities, a wide range of lubricant viscosities is required.

The dynamic viscosity of a fluid is its resistance to shearing flows where adjacent layers with different speeds move parallel to each other. It is expressed in the unit Pa.S (Pascal-second). On the other hand, the kinematic viscosity of a fluid is the ratio of its dynamic viscosity to the density, both measured at the same temperature. It is commonly expressed in the unit centistokes (cSt; 1 cSt = 0.01 Stoke), whereas its CGS unit is expressed as Stoke.SI unit of kinematic viscosity, meter square per second (m^2/s ; $1 \text{ m}^2/\text{s} = 10^6 \text{ cSt} = 10^4 \text{ St}$).

The viscosity of lubricating oil is also a function of temperature and it should vary as little as possible with the increase or decrease of temperature. It is, therefore, necessary to have some method of determining the viscosities of oils at temperatures other than those at which they are measured. Hence, two different temperatures are

selected (usually 40°C and 100°C) for measuring the viscosities and then plotting these points on special viscosity-temperature charts developed by ASTM (American Society of Testing and Materials)[42]. Viscosity index (VI) is an arbitrary measure to express the change of viscosity with temperature variations[43]. A low VI indicates a relatively high rate of change of viscosity with temperature i.e. it will thin out more at the higher temperature. On the other hand, a higher VI value signifies a lesser effect of temperature on viscosity i.e. the oil will thin out less with increasing temperature[44]. It has been found that the addition of certain oil-soluble polymeric materials to base oil can greatly improve its viscosity properties and thereby the viscosity index. The additives that improve the viscosity index of the oil are known as viscosity index improvers (VII) or alternatively known as viscosity modifiers (VM) [45-46]. VIIs keep the viscosity of the oil at a satisfactory level which provides stable oil film even at increased temperature.

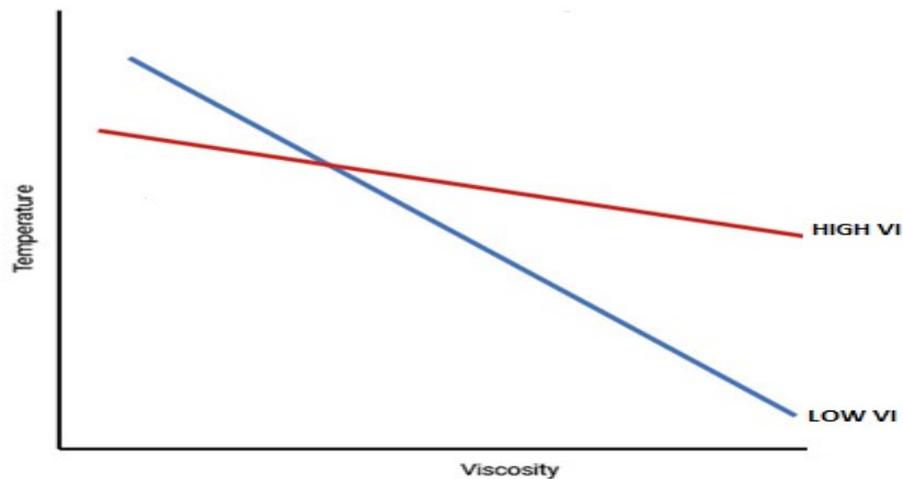


Figure 4: Temperature dependence of viscosity

Acrylate and methacrylate-based polymers are the most commonly used VIIs in lubricants[47]. Some of the other reported VIIs are poly isobutylenes (PIB), olefin copolymer (OCP)[48], ethylene α -olefin copolymers, styrene isoprene copolymer

(SIP), polybutadiene rubber (PBR), poly alkyl styrene[49], maleic anhydride based polymers, and even some vegetable oil-based polymers, etc[36].

The performance of an additive as VII depends on its molecular weight, chemical behavior, shear stability, and also on its solubility in the base oil[50]. The mode of action of VII was first established by Selby in 1958[51]. However, the report presented lacked any physical data supporting the proposed mechanism. Later, in a work of Flory, it was stated that the radius of gyration, R_g , of additive molecules depends on the interactions between the solvent molecules and the polymer chains. The affinity among the polymer chains, in a “poor” solvent, results in the collapse of the polymer chains into compact polymer globules. However, in the case of a “good” solvent, where repulsive forces act between the polymer chains, there occurs an expansion of the globule into random coils[52]. With the rise of temperature, an enhancement in the power of solvation is observed for the solvent and consequently, there occurs an increase in the polymer-solvent interaction. As a result, the polymer molecules further change their shape from tight coil to expanded random coil and thus offset the normal viscosity reduction with increasing temperature. The process of expansion of the coil is reversible as with decreasing temperature the coil contraction occurs[53-55]. Again, the increasing polymer content in the solvent increases the total amount of polymer globules in the solution bringing about a higher viscosity index for the oil.

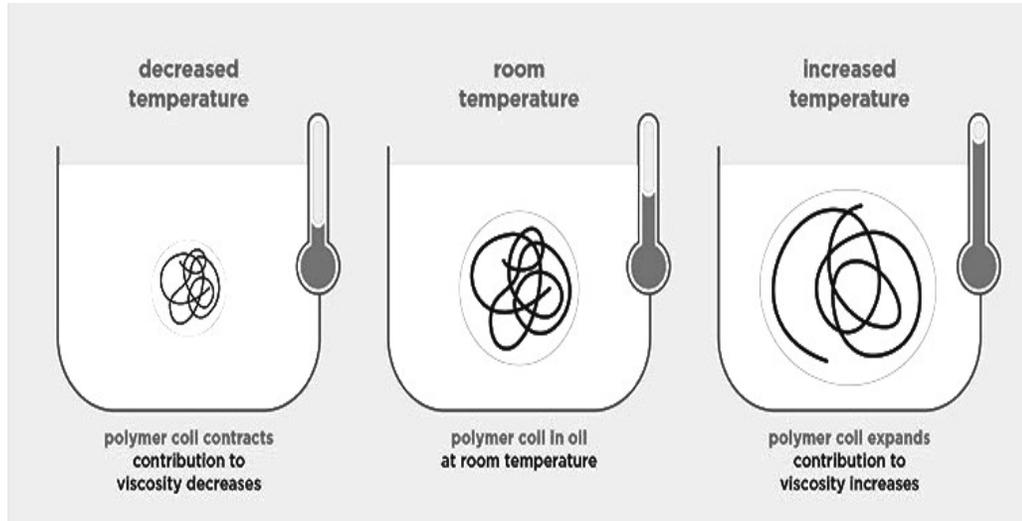


Figure 5: Coil expansion model of viscosity index improvers

The long molecules of the VIIs are also prone to degradation due to mechanical shearing in operating conditions. Under such conditions, the long chains of the VII change from a spherical coil orientation and align them in the direction of the stress thereby reducing the resistance to flow. But the chains return to their usual random arrangement once the stress is removed and, therefore, the viscosity loss is recovered. This condition is known as a temporary shear breakdown. But sometimes under the service conditions, due to polymer coil distortion in extreme conditions, the long chains undergo rupture to form small chains. The viscosity contribution by the smaller disintegrated molecules becomes less than that of the single parent molecule and they become less effective as VII. This condition is called permanent shear breakdown. Polymers of high molecular weight are more vulnerable to distortion while the polymers of sufficiently low molecule weight may not even undergo shearing. Therefore, the right combination of molecular weight and chain length is necessary to exhibit optimum stability.

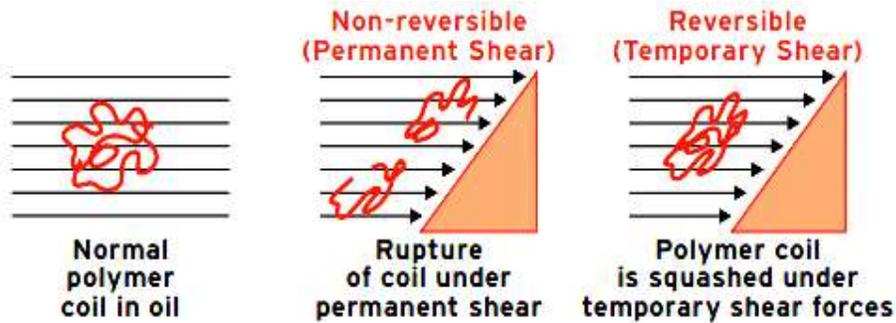


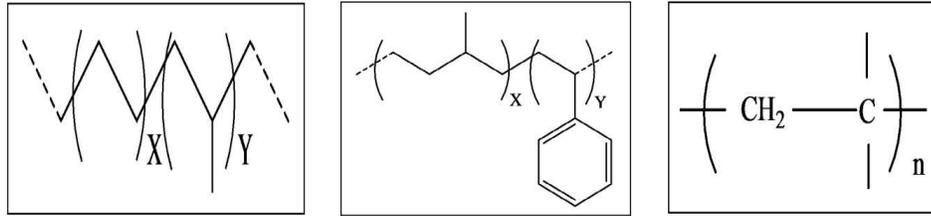
Figure 6: Temporary and permanent shearing of viscosity index improvers

Recently, a comprehensive report was presented by Michael J. Covitch *et al.*, about an improved model to correlate the polymer structures in solution with the rheological properties of a fluid. The experiment involves measurement of the polymer coil dimensions by the Small-Angle Neutron Scattering test and by intrinsic viscosity measurement. The critical assessment of the results indicated that the polymers which expand with temperature have greater viscosity index contributions than those that do not[52].

The viscosity of the solution also depends on the polymer and solvent chosen. At a very low concentration of the polymer, there is no strong interaction between polymer molecules. But as their concentration is increased, the increment in viscosity increases at a much faster rate. The following equation describes the dependence of concentration upon viscosity.

$$\eta = \eta_c \exp(\beta C)$$

where η is the dynamic viscosity, C is the concentration of the polymer, η_c and β are constants.



Ethylene-propylene copolymer (OCP), Styrene-isoprene copolymer (SIP), Polyisobutylene (PIB)

Figure 7: Structure of some commonly used viscosity index improvers

Most of the additives that are in use today work either as PPD or VII or reports regarding their multifunctional additive behavior are very few. But, with the advent of innovative technologies and to satisfy the growing OEM requirements and consumer needs, more is required out of an additive. This requires modification of the existing chemistry or manipulating the structure and architecture of the traditional additives. These variations not only improve their performance as PPD and VII but also boost their thermal stability.

- **TRIBO IMPROVER**

This type of additives is further classified into Friction modifiers (FM), Antiwear(AW), & Extreme Pressure(EP) Additives. FM s are acting low-temperature pressure load where AW s prevent wear in comparatively higher temperature pressure environment. A Stribeck curve in Figure:-9 showed that their effects overlap with each other[57].

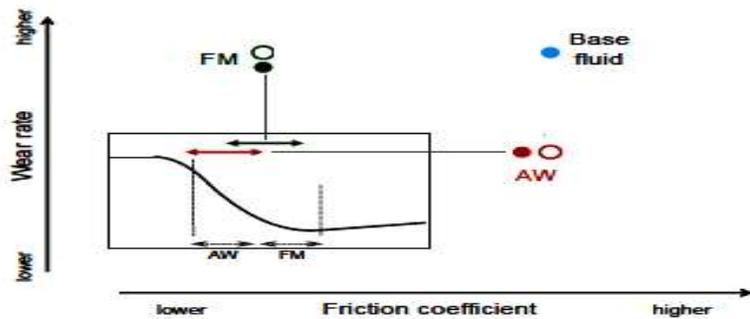


Figure 8: Overlapping effect of tribo improvers

Wear is the deformation of shape at the tribological contact. Wear is a natural process of continuous rubbing of metal parts in a machine. Zinc diethyldithio phosphate (ZDDP) is an effective friction modifier, antiwear, and antioxidant additive and is commonly used in several kinds of lube. The working mechanism of it as AW by surface analysis revealed the formation of inorganic compounds of Zn, S,&P whereas in comparatively low temperature and applied pressure range i.e. in moderate engine condition ZDDP mainly perform through adsorption and thus making a protective film[57].

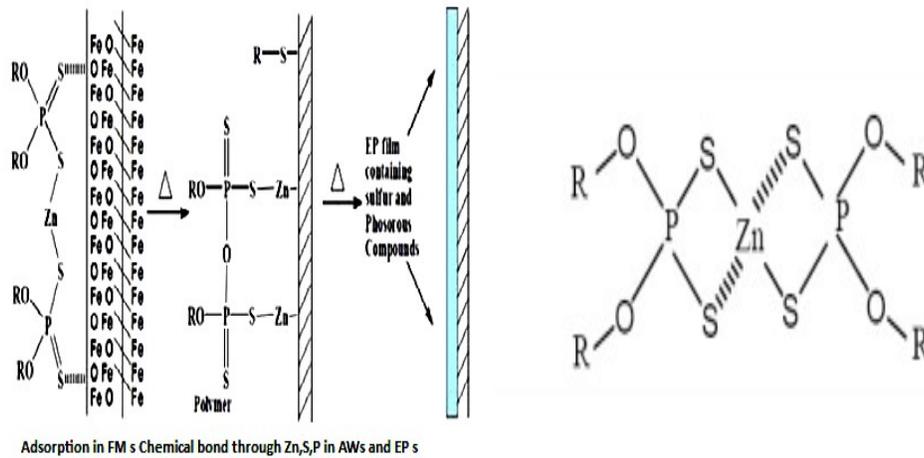


Figure 9: Chemical structure & working of ZDDP as FM's and AWs

The additives may work in an interface (AW, Dispersant,) or bulk(PPD, VII). They can act either chemically (EPs, AWs) or Physically (FM's, Dispersants). According to working function they can be further considered as Tribo-improver, Maintainers, or Rheo –improver relationship between different types of additives is summarised in Table:-2.

Working mechanism	Working site		
	Interface		Bulk
Chemically	Extreme Pressure additive	Anti wear agent	Corrosion Inhibitor
Physically	Dispersant	Anti foam agent	Demulsifier
			Detergent
			Anti-oxidant
			Pour Point depressant
			Viscosity modifier
Working function	Tribo improver	Maintainers	Rheo improvers

Table 2: Relationship of different kinds of additives according to the working mechanism, working site & working function[57].

• **THE OBJECTIVE OF THE PRESENT WORK**

The present work is concerned with the synthesis, characterization, and performance evaluation of some multifunctional organic polymeric additives as well as additives derived from vegetable oil polymer for lube oil and to evaluate the potential of chemically modified vegetable oils as alternate lube base stock. Acrylate, methacrylate based polymers were studied as multifunctional additive. Other molecules used in this study are vinyl acetate, styrene, 1-decene, and α pinene. Some biodegradable multifunctional lube oil additives based on vegetable oils (linseed oil, rapeseed oil, rice bran oil, and castor oil) have also been investigated. Vegetable oil indeed has a fairly high viscosity index and low-temperature flowability compared to mineral-based lube but these are thermally unstable and are prone to auto-oxidation as major fatty acid contains in triglyceride moiety contains unsaturation. Fatty acid composition of some common vegetable oil are summarised in Table 2, and properties of these oils are summarised in Table 3.

Vegetable Oils	C12:0	C14:0	C16:0	C18:0	C16:1	C18:1	C18:2	C18:3	Others
Soybean oil	-	-	11-12	3	0.2	24	53-55	6-7	-
Sunflower oil	-	-	7	5	0.3	20-25	63-68	0.2	-
Rapeseed oil	-	-	4-5	1-2	0.21	56-64	20-26	8-10	9.1 (20:1)
Palm oil	-	1	37-41	3-6	0.4	40-45	8-10	-	-
Rice bran oil	-	-	20-22	2-3	0.19	42	31	1.1	-
Cotton seed oil	-	1	22-26	2-5	1.4	15-20	49-58	-	-
Coconut oil	44-52	13-19	8-11	1-3	-	5-8	0-1	-	-
Corn (Maize) oil	-	-	11-13	2-3	0.3	25-31	54-60	1	-
Peanut/Ground nut	-	-	10-11	2-3	0	48-50	39-40	-	-
Sesame oil	-	-	7-11	4-6	0.11	40-50	35-45	-	-
Safflower oil	-	-	5-7	1-4	0.08	13-21	73-79	-	-
Karanja oil	-	-	11-12	7-9	-	52	16-18	-	-
Jatropha oil	-	1.4	13-16	6-8	-	38-45	32-38	-	-
Rubber seed oil	-	2-3	10	9	-	25	40	16	-
Mahua oil	-	-	28	23	-	41-51	10-14	-	-
Tung oil	-	-	2.67	2.4	-	7.88	6.6	80.46 *	-
Neem oil	-	-	18	18	-	45	18-20	0.5	-
Castor oil	-	-	0.5-1	0.5-1	-	4-5	2-4	0.5-1	83-85 #
Linseed oil	-	-	4-5	2-4	0-0.5	19.1	12-18	56.6	-
Olive oil	-	-	13.7	2.5	1.8	71	10	0-1.5	-

* Alpha-eleostearic acid. # Ricinoleic acid.

Table 3: Fatty acid composition of some common vegetable oils[56].

Vegetable Oils	Iodine Value	Pour Point (°C)	Cloud Point (°C)	Kinematic Viscosity at 40 °C (mm ² /s)	Flash Point (°C)	Density at 15 °C (g/cm ³)
Soybean oil	138-143	-12	-4	29	254	0.914
Sunflower oil	125-140	-15	-9.5	36	274	0.916
Rapeseed oil	98-105	-15	-2	35	246	0.912
Palm oil	48-58	23.6	25.2	39.4	252	0.919
Rice bran oil	103	13	16	38.2	184	0.906
Cotton seed oil	90-119	-4.5	-0.5	34	234	0.918
Coconut oil	8-11	12.7	13.1	27	266	0.918
Peanut/Ground nut/ Arachis oil	84-100	-7	4.5	40	271	0.903
Sesame oil	104-116	-11	-8	36	260	0.918
Karanja oil	81-90	-4	2	38.8	212	0.9358
Jatropha oil	82-98	-6	11	34	225	0.94
Rubber seed oil	104	18	25	33.89	228	0.928
Mahua oil	58-70	11	20	37.18	238	0.945
Neem oil	81	7	13	35.8	200	0.918
Castor oil	83-86	-21	-18	251	229	0.960
Linseed oil	168-204	-15	5	26-29	241	0.938
Safflower oil	145	-7	-2	28.3	260	0.914
Olive oil	75-94	-14	-11	39	177	0.918

Table 4: Physical properties of some common vegetable oils[56].

The oil we used in this study was Linseed oil, Castor oil, and Rapeseed oil as non-edible oil, and Soya bean, Sunflower, Ricebran, and Olive oil as edible oil. The additives (polymeric) were synthesized by thermal irradiation in presence of initiators like azobisisobutyronitrile (AIBN) or benzoyl peroxide (BZP). Another part of this study was to synthesize epoxidized vegetable oils(Linseed oil, Castor oil,

Olive oil, Soyabean oil, Sunflower oil) and subsequent epoxy ring-opening by different alcohols (2-ethyl hexanol, dodecanol, n-octanol, 1-decanol, dodecanol). Performance evaluation of these chemically modified vegetable oils revealed that they can be a replacement for mineral lube.

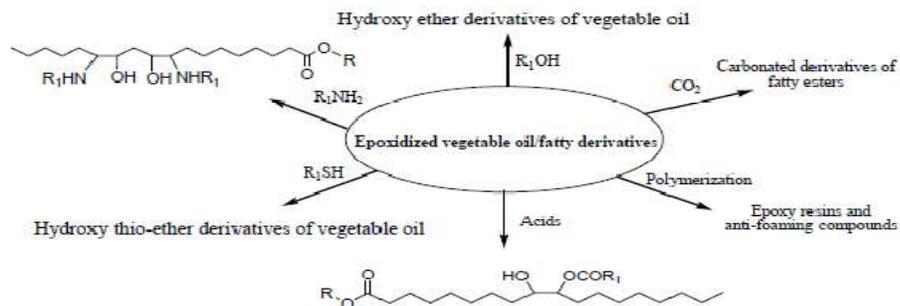


Figure 10: Different pathways to modify epoxy vegetable oil[56].

The additives, as well as modified vegetable oils, were characterized by spectral techniques ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and FT-IR), followed by molecular weight determination with gel permeation chromatography (GPC) and finally, assessment of their thermal stability was done by thermogravimetric analysis (TGA). The additives doped in mineral oil and modified vegetable oils were investigated for their performances as pour point depressant (PPD) and viscosity index improver (VII) as per the standard ASTM (American society for testing and materials) methods. Antiwear properties were ascertained by a four-ball wear test. Biodegradability analyses were also conducted for the vegetable oil-based additives by soil burial method and disc diffusion method to test their biocompatible nature.

REFERENCES

References are given in BIBLIOGRAPHY under “**General introduction**”.