GENERAL INTRODUCTION

Lubricants or lubricating oils are the substances introduced between two moving surfaces (sliding/rolling) to reduce the friction resistance between them. Lubricating oil has been used for a variety of purposes to prevent friction and corrosion on the clashing surfaces, suppress heat generation, keep objects clean and create insulation and rust-preventive effects [1]. Petroleum-based lube oil is a complex mixture of various substances like hydrocarbons, aromatic, naphthenic, paraffinic, etc. which have a molecular weight ranging from C_{20} –C_{50} with a boiling point range from 150^0C to 600^0C [2]. The effectiveness of lube oils solely depends on their rheological properties like viscosity index (VI) i.e. change of viscosity with the change of temperature, low-temperature fluidity, etc. That means a good lube oil should have a very minute change of viscosity with change in temperature [3] and must have flow character at high as well as low temperature [4]. With the development of modern engines and equipment, only the base oils can't fulfill all the requirements of the modern engine and equipment. As a result, scientists are trying to make lubricants that can fulfill most of the requirements of the modern engine and equipment. Research and developments show that only the base oil can't fulfill all the requirements of perfect lube oil. As a result, to improve the performance of lube oil, it is necessary to add some foreign substances, which are called lube oil additives [5]. When additives are added to the base oil then the mixture is called lubricants. Normally lubricants are synthetic polymeric or in some cases nonpolymeric in nature [1]. The additives blended lube oil or lubricants are more compatible with the modern engine. The additives not only increase the performance of the base oils that already present in them but also add some extra properties [6].

Additives perform a wide variety of functions within engine lubricants [6]. These are:

i. Protect the engine surfaces by performing anti-wear, anti-rust or anti-corrosive properties, which in combination prevent damage to the coatings and surfaces within the engine.

ii. Modify the physical properties of the lubricant by acting as viscosity modifiers and pour point depressants.

iii. Prevent and control the effects of engine deposition by acting as antioxidants and dispersants and detergents.

iv. Increased fuel economy by acting viscosity modifying properties which are due to reduction of friction between moving surfaces or providing favorable viscosity profiles that can lead to improved efficiency.

v. Reduce pollution by emerging new properties like biodegradability to the lube oil.

Based on the lubricant types different combinations of the quantity of additives are used and the amount of the additives to be added to the lube oil may reach up to 30% [7].

Different types of additives which are generally used in the petroleum base lube oil are: i) Pour Point Depressant (PPD), ii) Viscosity Index Improver (VII) or Viscosity Modifier (VM), iii) Friction Modifier (FM), iv) Anti-wear Additive (AW), v) Detergent, vi) Antioxidant (AO), vii) Extreme Pressure Additive (EP), vii) Dispersant, viii) Anti-foaming Agent, ix) Rust and Corrosion Inhibitor.

Pour Point Depressant:

The pour point of an oil is the lowest temperature at which an oil will pour or flow when cooled. Most of the lube oils contain some paraffin wax and complete removal of this paraffinic wax from the lube is not only difficult but also expensive. At low temperatures, the wax left in the lubricant base stock comes out of solution as wax crystals, producing a gel-like structure that impedes the flow of lubricant to critical engine parts which badly affects the performance of the engine [8], [9]. But whenever the pour point depressants are added, it will not reduce the amount of wax formed, but inhibit the formation of interlocking crystal networks; that means pour point depressant facilitates the flow property of the lube oil at low temperature [10], [11]. The polymeric additives which are used as pour point depressant have some pendant alkyl groups [12]. There must be an appropriate monomer-monomer ratio in the copolymers that are used as pour point depressants [14].

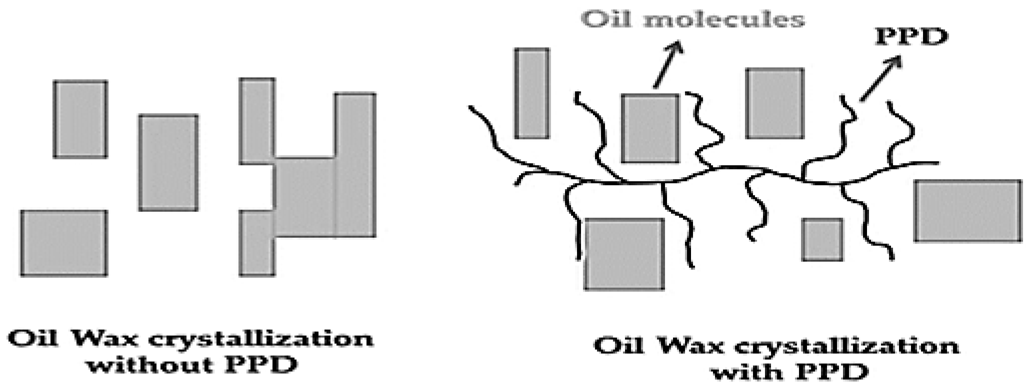


Figure 1: Action mechanism of pour point depressant

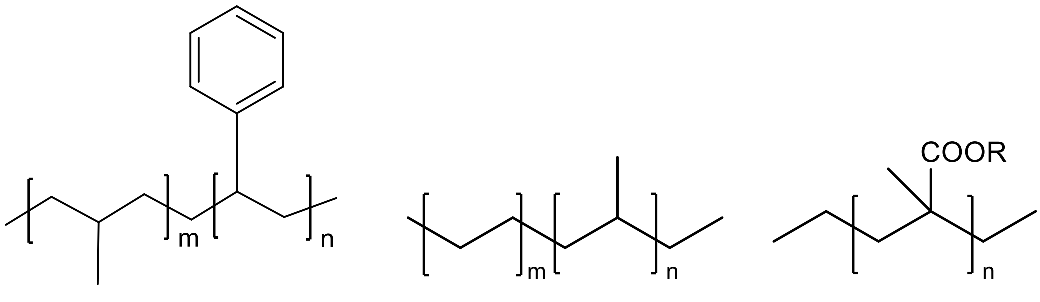
Polyalkyl acrylate, copolymers of polyalkyl methacrylate [15], maleic anhydride-based polymeric additives, high molecular weight vegetable oil-based polymers [16], acrylate-based zinc nanocomposite are widely used as PPD in lubricant base stocks.

Polyalkylacrylate **polyalkylmethacrylate**

Figure 2: Structures of some commonly used Pour Point Depressants

Viscosity Index Improver:

Viscosity Index (VI) is a unitless arbitrary number of a fluid that measures the change in viscosity with a temperature change. The lower value of VI indicates that viscosity is more affected by a change in temperature and on the other hand higher value of VI indicates that the change of viscosity is very less with temperature change. If the lubricant is too viscous, it will require a large amount of energy to move and if it is too thin, the surfaces will come in contact and friction will increase. Since in the automotive engine during working condition there is a huge change in temperature, the lubricant with lower viscosity index affect badly the engine performance and durability. So to modify the viscosity index of lube oil, there must be added some foreign substance which is called viscosity modifier (VM) or viscosity index improver (VII). VII resists the change of viscosity of lube oil with a change in temperature [17]. High molecular weight polymers like vegetable oil-based polymers, acrylate-based polymers, hydrogenated styrene isoprene copolymer, ethylene-propylene copolymer are widely used as VII.



Hydrogenated styrene isoprene copolymer ethylene-propylene copolymer (OCP) polyalkyl methacrylate

Figure 3: Structures of some commonly used viscosity index improver

This is to be believed that when the oil temperature is low, these polymers curl up into tight balls that flow readily with the oil molecules **(Figure 4)**. As the temperature increases, they expand into large stringy structures that restrict the normal oil flow, which has a thickening effect on the oil. When the oil cools down, the polymers go back to their original shape [18].

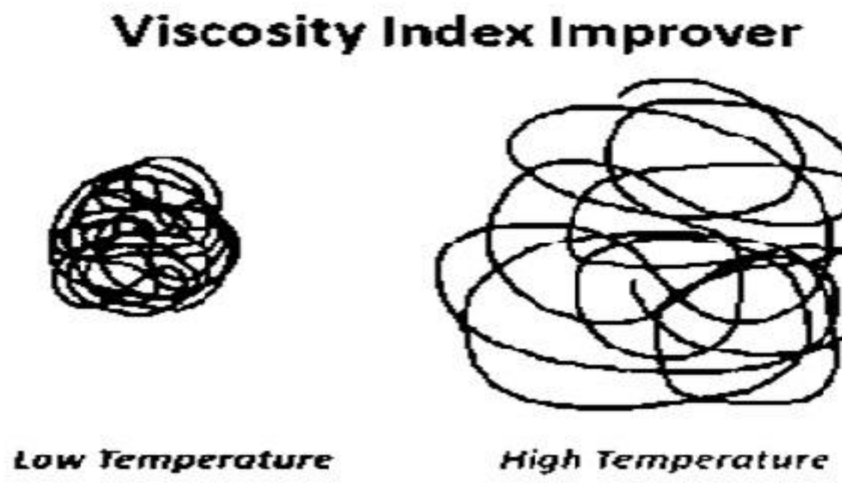


Figure 4: Effect of temp. of polymeric additive in lube oil

Friction Modifier:

Friction modifiers are the additives that are used in lubricants to modify the coefficient of friction (hence the name, Friction Modifiers). Friction modifiers are employed to prevent wear on metal surfaces. These additives help slow down wear and increase fuel economy. The mechanical action of the friction modifier is that they form a polar molecular film by strong adsorption on the surface of the metal. FMs are normally straight-chain hydrocarbons with a polar head group. Generally, the polar head groups are Carboxylic acids or their derivatives amines, amides and their derivatives, phosphoric or phosphonic acids, and their derivatives. The polar head groups are strongly adsorbed on the metal surface and form relatively strong bonds on the other hand the long hydrocarbon tail is left solubilized in the oil. Both the structure of the hydrocarbon chain and the nature of the polar head groups have a strong influence on the contribution to friction reduction. Polyol esters of fatty acids e.g. glyceryl monooleate, amides of fatty acids, molybdenum compounds e.g. molybdenum dithiocarbamate, sulfurised fats, and esters are the widely used friction modifier.

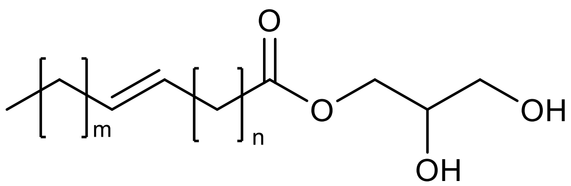


Figure 5: Glycerol monooleate (GMO)

***Anti-Wear Additives*:**

Lubricants form a hydrodynamic multimolecular film on the surface of the metal. When the load is low, the surfaces can't touch each other and which results no wear. However, the formation of a hydrodynamic multimolecular film on metal surfaces is not always possible.

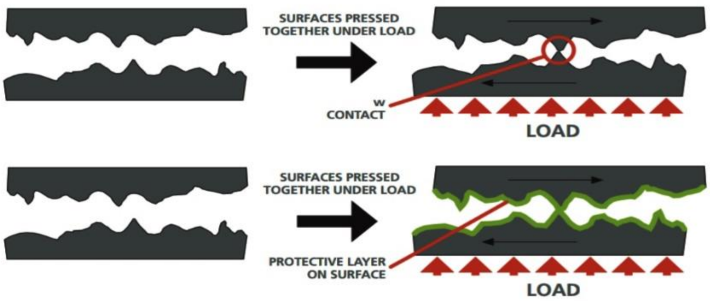


Figure 6: Action mechanism of anti-wear additives

When the load is high and the lubricant's viscosity is not good, the surfaces of the moving parts make contact, shown in **Figure 6**. This metal-metal contact between the lubricated surfaces destroys the boundary lubrication. Under this situation, friction can be minimized by the addition of the anti-wear additives to the metal surface by the formation of the lubricating solid film. Normally anti-wear additives strongly adsorbed or chemisorbed on the metal surface and form a film. When the chemisorption takes place, electrons transfer occurs between additive molecules and metal surfaces [19].

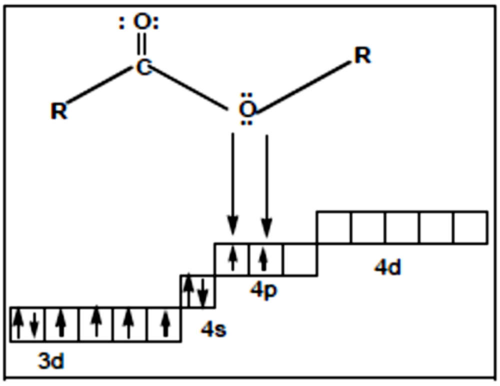


Figure 7: Donor accepter bond between AW additive and metal (Fe) surface

Some examples of anti-wear additives are zinc dithiophosphate (ZDP), zinc dialkyl dithiophosphate (ZDDP) are used in formulated engine oils [20]. Some Organosulfur, Organophosphorus compounds are used as AW as well as EP additives. It has been found that acrylate-based ZnO nanocomposite, polymeric vegetable oils can also be acted as AW.

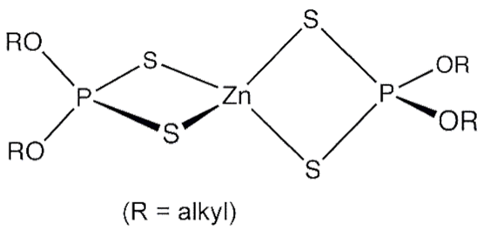


Figure 8: Structure of a monomeric zinc dialkyl dithiophosphate

Detergent and Dispersant Additives:

During the combustion process in the internal combustion engine, several strong acids are formed in the engine oil and deposited on the metal surface [21]. Detergents are substances that neutralized the acids from on the metal surface. Sulfonates, Phenates, Salicylates, phosphates of alkaline earth metals such as Ca and Mg are used as detergent. Heavy metals like Ba are no longer used. Dispersants have ionizable polar heads and hydrocarbon chains that form micelles and trap soot or sludge and also stabilize larger particles by charge repulsion. By which dispersant additives keep the foreign particles in a finely divided and uniformly dispersant through the lube oil [22].

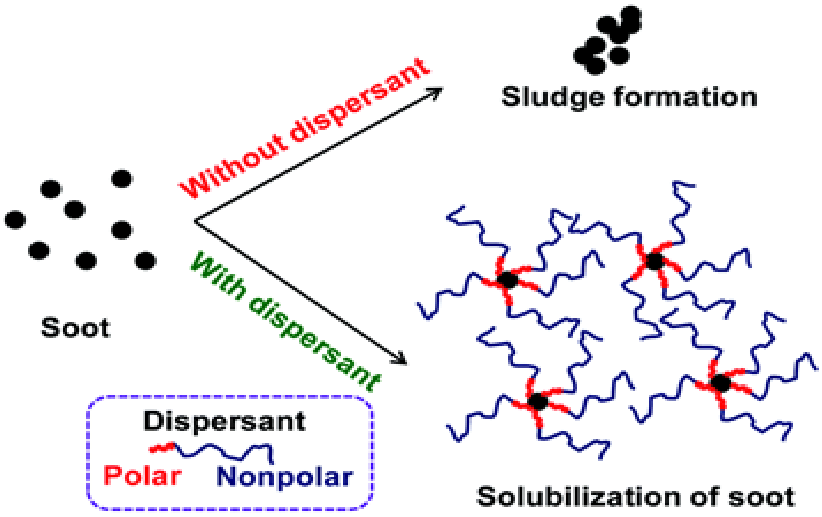


Figure 9: Action mechanism of dispersant additive

A dispersant molecule has a polar head and the polarity is derived from oxygen or nitrogen moieties and a hydrocarbon tail which is normally polyisobutene, which enables the substrate to be fully oil soluble. Some widely used dispersants are Mannich base and phosphosulphurized Mannich bases of hindered phenols [23], polyisobutylene succinimides [24], amidation products of maleic anhydride and alpha-olefin copolymer [25], etc

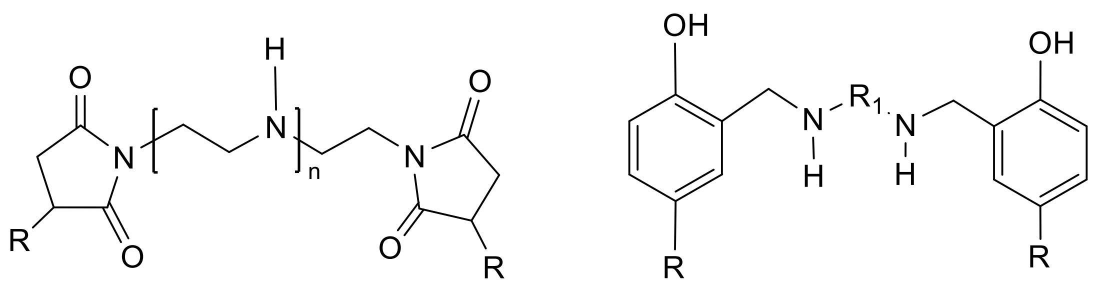


Figure 10: General structure of a succinimide based and Mannich Base dispersants

Antioxidant Additives:

Oxidation of lube oil makes the oil dark and thick. Because during oxidation hydrocarbon chains of lube oil are broken down and form insoluble soot or sludge particles. Because of the oxidation of lube oil, several organic acids are produced which are extremely corrosive towards non-ferrous metals and further oxidation leads to the buildup of polymeric material. These high molecular weight oxygenated polymers cause oil thickening, varnish, and gum deposits on pistons and other engine components.

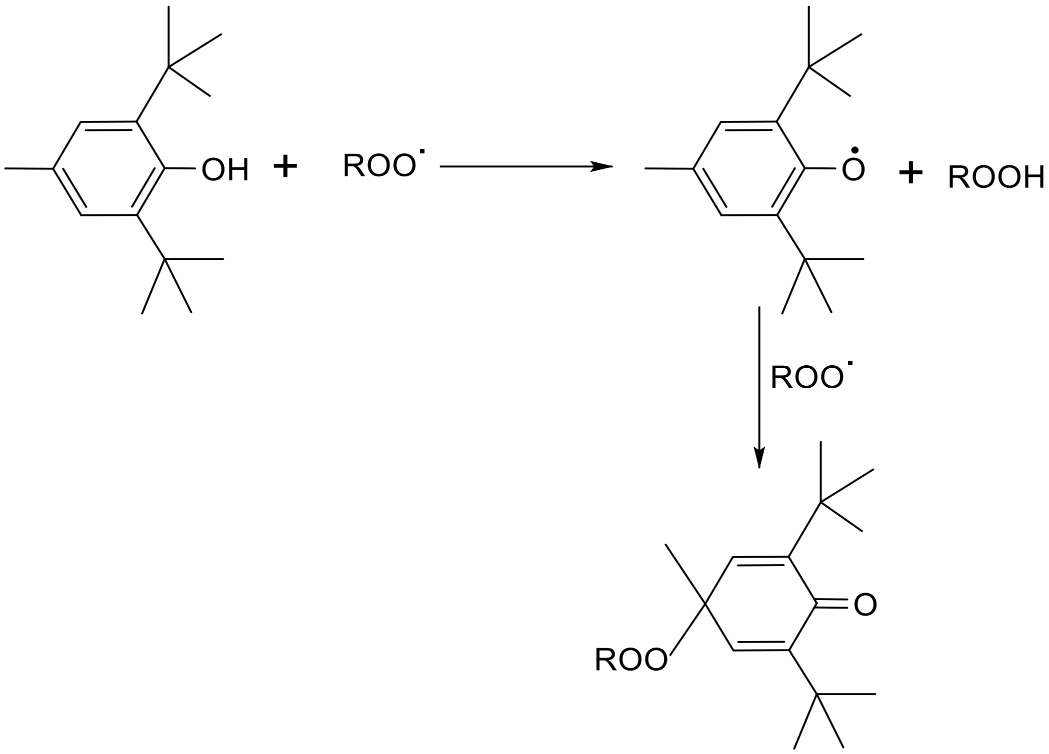


Figure 11: Radical trapping by hindered phenols

Antioxidants work by disrupting the chain propagating steps of the oxidative process by which these insoluble species are formed. The oxidative process is a chain reaction which once started, propagates at an exponential rate producing increasing amounts of free radical or peroxide species [6]. The antioxidants themselves function as either peroxide decomposers or as free radical traps. Zinc dialkyl dithiophosphate **(**ZDDPs) can act as antioxidants by destroying the chain propagation steps of the oxidative reaction, by acting as either peroxide decomposers or free radical traps. Hindered alkyl phenols can break down free radicals chain reaction to form stable hindered radicals which are not able to propagate the free radical chain reaction **(Figure 11)**.

Although many researchers have studied and reported several additives which are functioning either only as a viscosity modifier [26] or pour point depressant [27] or anti-wear additive [28] or some additives work based on bifunctional properties like viscosity modifier and pour point depressant [29] or viscosity modifier and anti-wear [30] or antioxidants and detergents/dispersants [31] etc. But the research based on polymeric additives that have multifunctional properties is very scanty to date. With the development of engine technology, the modern engines are demanding cost-effective, high quality and environmentally benign additive which have multifunctional performance [32]-[34]. Keeping these in mind, the author has made an effort to form some multifunctional additives in a single additive system to fulfill the above demand. Some acrylate-based like dodecyl acrylate, behenyle, and isodecyl acrylate ionic liquid blends were synthesized and multifunctional additive performance was also evaluated. Keeping in mind, the concept of green technology, the present investigation also comprises the synthesis and evaluation of the performance of vegetable oil-based multifunctional additives. The vegetable oils used in this study are castor oil, rapeseed oil. Our present investigation also comprises the synthesis of acrylic base ZnO nanocomposites as lube oil additives. The additive doped lube oils show excellent multifunctional additive performance along with excellent biodegradability. In brief, the thesis emphasizes on the synthesis of additives followed by characterization as well as performance evaluation of the synthesized additives for lubricating oils. The characterization was carried out by spectroscopic method, especially FT-IR and NMR. Thermogravimetric (TGA) was used to determine thermal stability. The gel permeation chromatographic (GPC) method was used to determine the molecular weight of the polymers. The characterization of nano-ZnO was performed by CEM, X-RD, and DLS. Finally, the performance of the additives mainly as viscosity modifier (VM), viscosity index improver (VII), pour point depressant (PPD), in few cases anti-wear (AW), antioxidant, and detergent/dispersant was evaluated by standard ASTM method in different base oils. The shear stability of some of the additives was also determined and deported. Biodegradability character was carried out by soil burial test method [35] and disc diffusion method using different fungal pathogens according to ISO 846:1997 rules. To study the mechanism action of pour point, photomicrographic image and power XRD of some of the PPD was carried out. The outcome of our present investigations has some important potential additives for lubricating oil which will be dealt with for commercial application and that will be taken up by our group in near future.

References

References are given in *BIBLIOGRAPHY* under "General Introduction" (Page No. 133-136)