General Introduction of Present Investigation

Lubricating oil is the basic building block of a lubricant. Lubricating oil is also known as base oil or lube oil. They are intricate mixture of paraffinic, naphthenic and aromatic hydrocarbon with a broad range of molecular weight, varying viscosity, density etc. The principal application of the lube oils is to reduce friction between metal surfaces which are on continual movement in an engine. In addition to friction reduction, lube oil plays a few varieties of functions in an engine e.g. resistance of oil viscosity with variation of temperature, improve flow properties at low temperature, less fuel consumption, corrosion inhibition and so on. Such massive work load led to lack of quality performance and eventually repeated oil change is required. With the advancement of technology and different kinds of modern engines, demands for technically better lube oil are mounting which embrace multifunctional performance, cost effectivity along with biodiversity protection. Natural petroleum based lube oils are incompetent to meet all the requirement of modern engine. Therefore to improve the performance of base oil, a huge number of functional additives[1-6] is added in lube oil. They not only improve the performance of base oil that already present on it but also introduce some new additional properties. These species are called lubricating oil additives and the additive incorporated lube oil is termed as commercial lubricant. The additives are generally chemical compound which are used as single chemical or blend of two or more compounds in base oil in varying range of concentration according to their requirement and field service performance. Most of the additives generally have long chain hydrocarbon unit in their structure to make them soluble in base oil.

Lubricant additives mainly fall into three general categories:

a) **Protect the lubricated surface:** These additives protect the lubricated metal surface from rust or wear by forming a protective film on them. Extreme pressure, [1] friction modifier, corrosion inhibitors, [2] anti-wear [3] (AW) etc are examples of this kind.

b) **Protect the base oil:** These kinds of additives protect the base oil as well as the additives from oxidation, high temperature cracking etc. Antioxidant [4] and foam inhibitors [5] are of this type.

c) **Improve the base oil performance:** These additives are used to introduce some new and useful performance to the lubricant or to enhance the already existing properties of base oil. Viscosity modifier (VM),[6] pour point depressant (PPD),[7] detergent, dispersant, demulsifier[8] etc. are common of these kinds of additives.

The present investigation includes the syntheses of some polymeric VM, PPD and AW additives, followed by their characterization and performance evaluation in base oils.

Concise backgrounds of these three types of additives are represented below.

♦ **Viscosity modifiers:** Viscosity is the most important single property of lubricating oil. For satisfactory performance of any kind of equipment, the first essential condition is to use an oil of suitable viscosity to meet the operating conditions. In selecting the proper lubricating oil for a particular application, viscosity is a primary concern. The viscosity of any fluid varies with temperature, decreasing as the temperature is increased, and increasing as the temperature is decreased. Viscosity index improvers (VII) or viscosity modifier (VM) are substances that oppose the variation of viscosity with temperature. They increase the viscosity of lube oil at higher temperature and minimize the increase of viscosity of oil at low temperature, thus maintaining a favourable relation between temperature and viscosity. The change of viscosity with variations in temperature is quantitatively express by an arbitrary number called Viscosity index [9] (VI). The higher value of viscosity index indicates the low rate of viscosity change of the oil with temperature variation and vice versa. The performance of viscosity improvers depends on their solubility in base oils, molecular weight, chemical behaviour and shear stability.[10] VIIs are long chain, high molecular weight polymers which perform by causing the relative viscosity of an oil to raise more at high temperature than at low temperatures. Usually this result is owing to an alteration in the polymer's physical configuration with rising temperature. It is postulated that at low temperature the polymer molecules remain in a coiled form so that their consequence on viscosity is minimized in base oil. As temperature increases the polymer molecules tend to straighten out, and the interaction among these long molecules and the oil results a proportionally greater thickening effect and thus effective volume is also increases.[11] This expansion of polymer coils with rise in temperature donate more and more viscosity to the oil. The coil expansion process is completely reversible as coil contraction occurs with falling temperature.

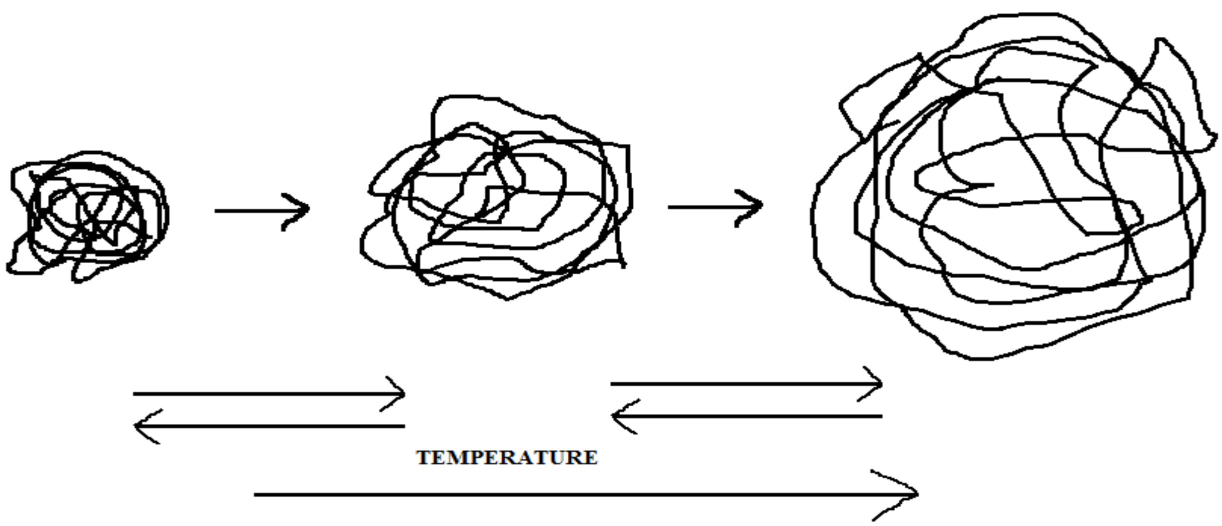


Figure 1: Polymer coil expansion with temperature

This increase in volume of polymer molecules (VM) causes increase of base oil viscosity which counterbalances the normal reduction of base oil viscosity with rise in temperature.[12] The VM of higher molecular weight also increases effective volume in oil solution and shows higher viscosity index value. A good VM should be more effectual in increasing the viscosity of oils of low viscosity and low effectual as the viscosity of base oil increases. By proper lubricant formulation it is possible to create an engine lubricant which fulfils both the low and high temperature demand of the SAE viscosity classification system.

The most commonly reported VM's are methacrylate polymers and copolymers, acrylate polymers, polyisobutylene (PIB), [13] olefin copolymer (OCP), styrene butadiene copolymers, hydrogenated styrene isoprene copolymer (SIP), polybutadiene rubber (PBR) etc.

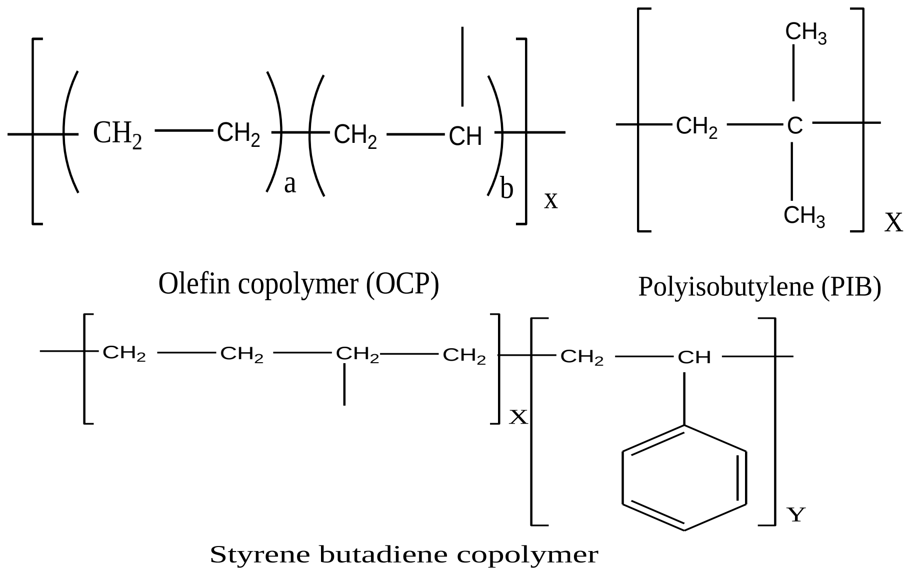
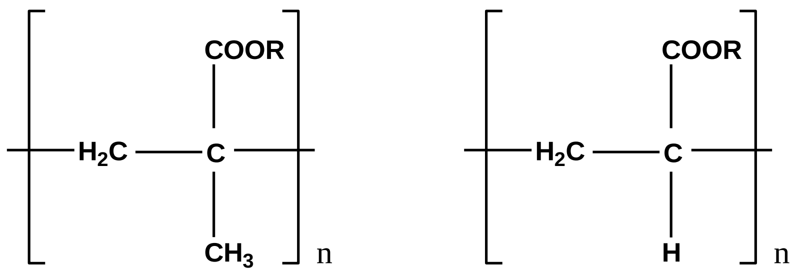


Figure 2: Structure of commonly used viscosity modifiers

Pour point depressant: Crude oil contains paraffin waxes (linear high molecular weight hydrocarbon), which tend to be separated from oil at a definite temperature (the cloud point). Paraffin wax deposition at low temperature is one of the serious and long-standing troubles in petroleum industry. At low temperatures, wax crystals easily form solid cakes, which can block filters and in the end lead to engine malfunction. As the temperature decreases the process of crystal growth increases and at a particular temperature the oil stops flowing. The lowest temperature at which oil can flow freely under its own weight is called pour point. To improve the fluidity at low temperature, pour point depressant (PPD) or lube oil flow improver's additives are used. It has been found that, by the addition of additives the shape of wax crystal modified. Various postulates have been suggested to explain this phenomenon and to steer the PPD product design. Among the various mechanisms nucleation, adsorption co-crystallisation and improved wax solubility are extensively accepted by mechanism researchers.[14, 15] A low pour point is mostly important for suitable performance of lubricants in cold climates. Most common PPD's are fumerate/ vinyl acetate copolymers, [16] polymethacrylates, [17] polyacrylates [18] etc.



Polymethacrylate **Polyacrylate**

Figure 3: Commonly used pour point depressants

This wax crystal networks also increase the oil viscosity and the consequence is usually momentary as a normal combustion engine can create sufficient shear to disrupt the wax. But this increases the workload on the engine and reduces its lifetime. Pour point depressants are polymeric compounds that constitute a long hydrocarbon chain with a polar part. The long hydrocarbon chain provides interaction between paraffin and the additive. The polar part is accountable for wax crystal morphology modification, inhibiting the crystal growth stage.

Anti-wear additive: Anti-wear additives formulated for lubricating oil to prevent direct metal-to-metal contact between parts of gears. These are act as boundary lubrication additives. Continuous friction between metal parts produces wear on metal surfaces which trim down the engine performance for long period of application. These wear and surface damage induced by the friction in moving parts in an engine can be decreased by anti-wear additives. Anti-wear additives form a surface film by tribochemical reaction to reduce wear between metal surfaces. Potent AW additives adsorb strongly or chemisorbs onto metal surfaces. In case of chemisorptions sometimes electron transfer occurs between absorbed molecule and metal surface[19] (**Figure 4**).

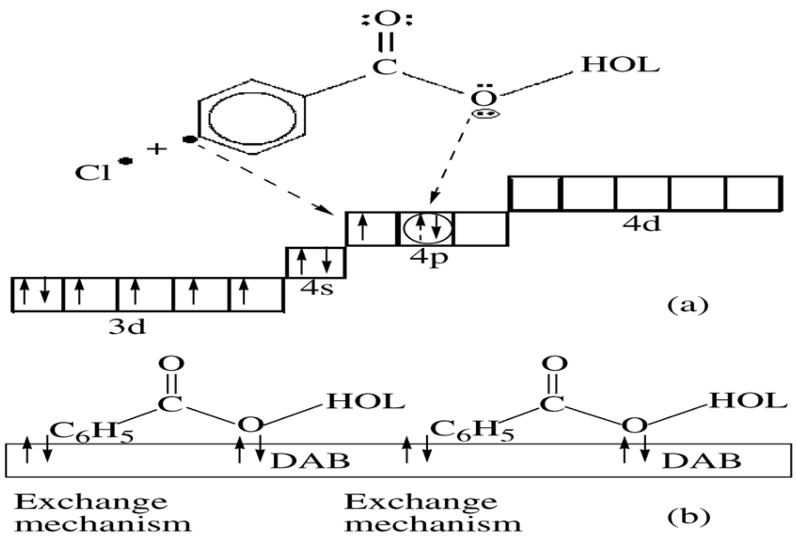
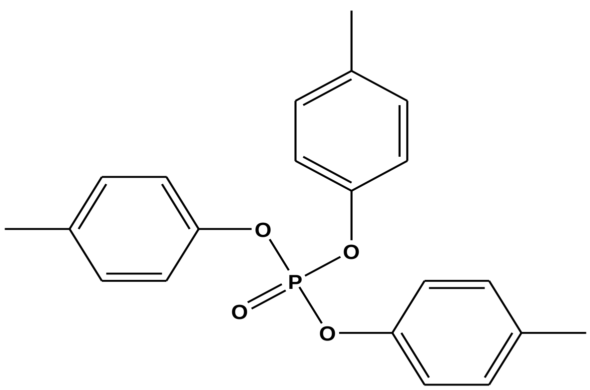
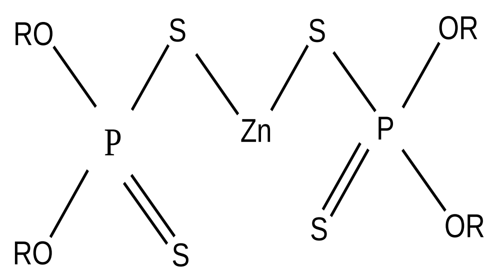


Figure 4: Schematic representation of (a) donor-accepter bond and (b) chemisorptions between AW additive (cholesteryl based) and metal (Fe) surface

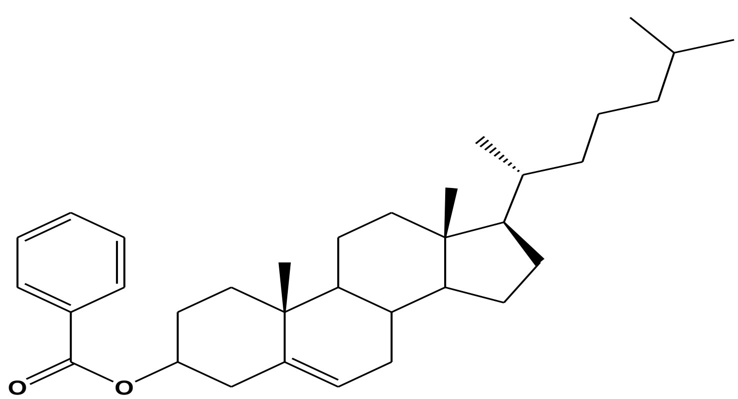
Among a range of compound organic phosphates, polysulfide, dithiocarbamates are extensively used AW and extreme pressure additive.[20] However, the most important progress in anti-wear chemistry was happened with the discovery (during the 1930s and 1940s) of zinc dialkyldithiophosphate (ZDDP), which is rapidly became the most extensive AW additive in formulated engine oils.[21] This also functions as a corrosion inhibitor and antioxidant. Researchers revealed that ZDDP breaks down and turns into a “tribofilm,” a thin, solid layer that sticks to the surfaces in contact and protects them from wear. Stearic acid is an effective AW additive under milder condition (under 150°C). Tricresyl phosphate (TCP) is also used for high-temperature operation as AW and EP additive in turbine engine lubricants, and also in some crankcase oils and hydraulic fluids. Dithicarbamates and dithiophosphate are complex organic molecules having sulfur and phosphorous elements. These two elements are well-known poisonous for catalytic converters. Moreover, only at high temperature these compounds are active. This means a critical phase in cold starts of engines. Because of hazardous nature of the above compounds in recent times liquid crystals [3] and nano particles [22] are used as AW additive. Both of them have suitable structural characteristics which facilitates them to cover metal surfaces by absorption or even chemisorptions.



Tricresyl phosphate



Zinc dithiophosphate



Cholesteryl benzoate

Figure 5: Some anti-wear additives

A lot of exciting studies have been accepted to elucidate the mechanism of anti-wear additives. Extreme pressure additives form stable protective films by thermo chemical reaction with the metal surfaces. This film can combat extreme temperature and mechanical pressure, thereby protecting metal surface.

A number of additives have been studied and reported to perform either only as a VM [23] or PPD [24] or AW [25] additive or little more based on offering bi-functional performance like VM-PPD [26] or VM-AW [27] etc, but literature concerning multifunctional performance of additives system are very meager till date. With the development of modern engines and technologies, cost effective and eco-friendly additives [28-30] imparting multifunctional performance is in great demand. In this connection for the development of lubricating oil additives attempts were made to insert multifunctional performance in a single additive system to meet the above demands. Liquid crystal blended polyacrylate systems were synthesised and evaluated as potential multifunctional additive. Noticeably very little amount of liquid crystal compound was used to ensure cost benefit. Looking into the concept of greener technology, the present study also includes synthesis and performance evaluation of vegetable oil based multifunctional additives. Vegetable oils used in the study are citral oil and rice bran oil. The nanoparticles used in the study are zinc oxide (ZnO) and magnetite (Fe_3O_4). The formulated lubricating oil additives showed excellent multifunctional performance in addition to very significant biodegradability.

In brief the thesis comprises synthesis, characterization and performance evaluation of a broad variety of different chemical additives for lube oils. The characterization was carried out spectroscopically (by FT-IR and NMR) followed by determination of thermal stability through thermo gravimetric analysis (TGA). Molecular weight of the polymers was determined by viscometric analysis or by gel permeation chromatographic method (GPC method). Finally performances of the additives chiefly as viscosity modifier (VM), pour point depressant (PPD) and anti-wear (AW) were assessed by standard ASTM methods in different base stocks.

Thickening property of some of the prepared additives were also determined and reported. Biodegradability study was performed by disc diffusion method using different fungal pathogens and by soil burial test as per ISO 846: 1997 rules. The outcome of the present study has yielded some potential additives which can be processed for commercial application and will be the carry on by our group in near future. Additionally, the study has also contributed a lot to the little known lube oil additive chemistry and will unquestionably help to cultivate research interest among the young scientists in the area of lubrication technology.

References

References are given in BIBLIOGRAPHY under General introduction of present investigation (PP 148-151).