# General introduction of present investigation

Lubricating oil, also known as base oil or lube oil is the primary building block of a lubricant. They are complex mixture of paraffinic, naphthenic and aromatic hydrocarbon with a wide range of molecular weight, varying viscosity, density etc. The first and foremost application of the lube oils is to reduce the friction of one metal surface on another during movement in engine.

Along with friction reduction, lube oil has to perform quite a few variety of functions in an engine e.g. less variation of oil viscosity with temperature, low temperature flow ability, less fuel consumption, corrosion inhibition and so on. Such huge work load led to poor performance and subsequently frequent oil change is required. With the improvement of technology and varying kinds of modern engines, more and more demands for technically improved lube oil are increasing which include multifunctional performance, cost effectivity along with environmental protection. Natural petroleum based lube oils are incapable to satisfy all the demand of modern engine. As a result a large number of functional additives [1-6] are added in lube oil to enhance the properties already present and to introduce additional performance. These compounds are called lubricating oil additive and the additive doped lube oil is termed as commercial lubricant. The additives are used as single chemical or mixture of two or more compounds in base oil in different concentration according to their need and field service performance. Structurally most of the additives have long chain hydrocarbon unit to make them soluble in base oil.

Broadly lube oil additive can be divided in three categories:

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

b) **Lubricant protective additive:** Lubricant protective additives protect the additives in lube oil from oxidation, high temperature breakage etc. Antioxidant[4] and foam inhibitor[5] are of this type.

c) **Performance enhancing additive:** These additives are used to introduce new performance or to enhance the existing properties of base oil. Common additives are viscosity modifier (VM),[6] pour point depressant (PPD),[7] detergent, dispersant, demulsifier[8] etc.

The present investigation comprises the syntheses of some polymeric VM, PPD and AW additives, followed by their characterization and performance evaluation in base oils. Brief backgrounds of these three types of additives are depicted below.

- **Viscosity modifiers:** Viscosity modifier (VM) or viscosity index improvers (VII) are substances that resist the change of viscosity with temperature. They increase the lube oil viscosity at high temperature and minimise the increase of oil viscosity at low temperature, thus maintaining a favourable relation between viscosity and temperature. Viscosity index[9] (VI) is an arbitrary measure to express the change of viscosity with variations in temperature. The higher the viscosity index, the smaller is the change of viscosity of the oil with temperature and vice versa. VI is used to characterize viscosity changes with relation to temperature in lubricating oil. The performance of VM depends on solubility of the additive in base oil, chemical behaviour, molecular weight and shear stability.[10] At low temperature the VM remain in a coiled form in base oil. With increasing temperature the coil get swollen by the lube oil and open up in chain like configuration, which has greater volume.[11]

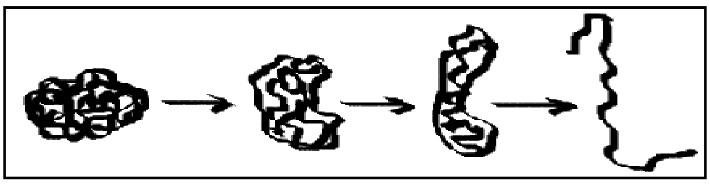
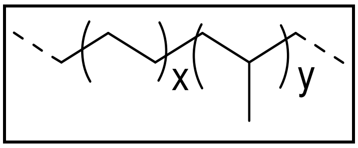
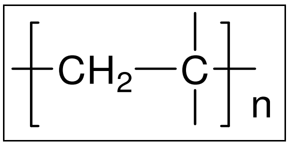


Figure 1. Expansion of VM with temperature

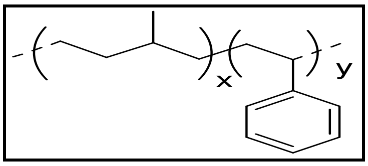
This increase in volume of the additives causes increase of base oil viscosity which offsets the normal reduction on base oil viscosity with higher temperature.[12] Higher molecular weight of the VM also increases effective volume in oil solution and shows greater viscosity index. A good VM should be more effective in increasing the viscosity of low viscosity oils and less effective as the base oil viscosity increases. By suitable formulation it is possible to make an engine lubricant which satisfies both the low and high temperature requirement of the SAE viscosity classification system. Most commonly reported VM's are polyisobutylene (PIB),[13] olefin copolymer (OCP), hydrogenated styrene isoprene copolymer (SIP), polyacrylates, polybutadiene rubber (PBR) etc.



Ethylene-propylene copolymer (OCP)



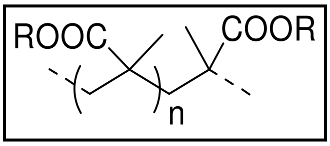
Polyisobutylene (PIB)



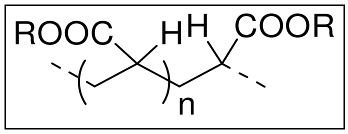
Hydrogenated styrene-isoprene copolymer (SIP)

Figure 2. Structure of commonly used viscosity modifiers

- **Pour point depressant:** Natural base oils always contain some wax (linear high molecular weight hydrocarbon), which at a specific temperature (the cloud point) begin to crystallize. The needle shaped crystals need very little wax to form solid grease like matrix, which immobilize the oil. As the temperature decreases this process of crystal growth increases and at a particular temperature the oil stops flowing. The lowest temperature at which oil can flow is called pour point. Pour point depressant (PPD) or lube oil flow improvers are additives which improve the low temperature fluidity of oil by decreasing the pour point. A low pour point is particularly important for proper performance of lubricants in cold climates. Most common PPD's are fumerate/ vinyl acetate copolymers,[14] polymethacrylates,[15] polyacrylates[16] etc.




Polymethacrylate




Polyacrylate

Figure 3. Commonly used pour point depressants

The wax crystal networks of the oil also lead to an increase in oil viscosity. This effect is generally temporary as a normal combustion engine can generate sufficient shear to disrupt the wax. But this can cause extra workload on the engine and decrease its lifetime. Pour point depressants are polymeric compounds with long hydrocarbon chain. Their structural linearity assists them to get aligned according to the oil wax network and inhibits the crystal growth.

- **Anti wear additive:** Anti wear additives, are additives for lubricants which prevent direct metal-to-metal contact between parts of gears. Constant friction between metal parts causes wear on metal surfaces which reduce the engine performance for long term use. AW additives reduce wear between metal surfaces by forming a protecting film. Powerful AW additives adsorb strongly or chemisorbs onto metal surfaces. In case of chemisorptions sometimes electron transfer occurs between absorbed molecule and metal surface[11] (**Figure 4**).

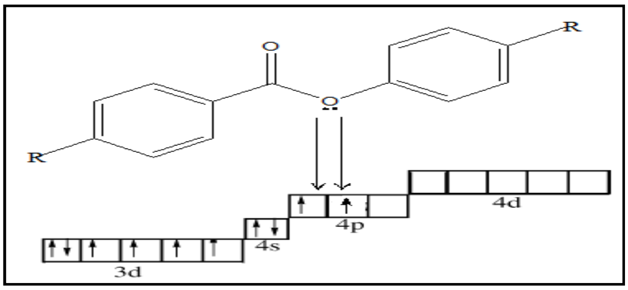
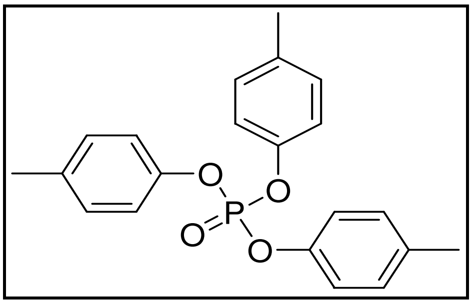
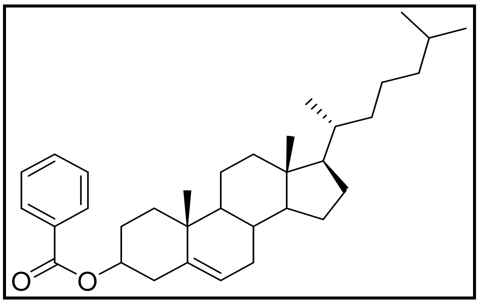



Figure 4. Schematic representation of donor accepter bond between AW additive and metal (Fe) surface

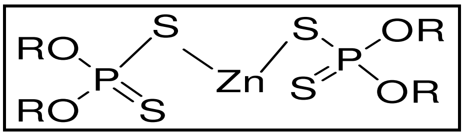
Organosulfur, organo phosphorus compounds e.g. organic polysulfide, phosphates, dithiocarbamates are widely used AW and extreme pressure additive.[17] zinc dialkyl dithio phosphate (ZDDP) is probably the most widely used AW additive in formulated engine oils,[18] also acts as a corrosion inhibitor and antioxidant. Tricresyl phosphate (TCP) is used for high-temperature operation as AW and EP additive in turbine engine lubricants, and also in some crankcase oils and hydraulic fluids. Stearic acid is also an effective AW additive under milder condition (under 150 °C). Due to hazardous nature of the above compounds recently liquid crystals[3] and nano particles[19] are used as AW additive. Both of them have favourable structure which assists them to coat metal surfaces by absorption or even chemisorptions.



Tricresyl phosphate



Cholesteryl benzoate



Zinc dithiophosphate

Figure 5. Some anti wear additives

Many interesting studies have been undertaken to explain the mechanism of anti wear additives. Extreme pressure additives form strong durable protective films by thermo chemically reacting with the metal surfaces. This film can withstand extreme temperature and mechanical pressure, thereby protecting metal surface.

Although people have studied and reported number of additives working either only as a VM[20] or PPD[21]or AW[22] additive or few more based on offering bifunctional properties like VM-PPD[23] or VM-AW[24] etc, but literature regarding systems showing multifunctional properties are very scanty till date. With the development of modern engines and advanced technologies, cost effective and eco-friend additives[25-27] providing multifunctional performance is in great demand. Keeping these views in mind attempts were made to introduce multifunctional performance in a single additive system to meet the above demands. Liquid crystal blended poly acrylate systems were synthesised and evaluated for multifunctional additive performance. Considerably lower amount of liquid crystal was used to ensure cost benefit. Looking into the concept of greener technology, the present investigation also includes synthesis and performance evaluation of vegetable oil based and other green monomer based multifunctional additives. Vegetable oils used in the study are olive oil, rice bran oil and peanut oil. Other green monomers used in the investigation are naturally occurring α pinene and β pinene. The additive doped lube oils showed excellent multifunctional additive performance in lube oil along with very significant biodegradability.

In brief the thesis includes synthesis, characterization and performance evaluation of a wide variety of different 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 mainly as viscosity modifier (VM), pour point depressant (PPD) and anti wear (AW) were evaluated by standard ASTM methods in different base oils. Degradation stability (in terms of shear stability) and oil 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 investigations has yielded some potential additives which can be processed for commercial application and will be the taken up by our group in near future. In addition, the investigation has also contributed much to the little known lube oil additive chemistry and will definitely help to grow research interest among the young scientists in the field of lubricant technology.

**References**

References are given in BIBLIOGRAPHY under General introduction of present investigation (PP 205-207).