General Introduction of Present Investigation

The principle of supporting a sliding load on a friction reducing film is known as lubrication. The substance of which the film is composed is a lubricant, and to apply it is to lubricate. From the early days of civilization people were used animal fat, mud, grease, oil etc. to assist in reducing the energy needed to slide one object against another[1]. So, the use of lubricants is not new concept but scientific focus on lubricants and lubrication technology is relatively new. It is recorded that have been utilized as lubricant as early as 2400 B.C.

Lubricating oil, also known as lube oil or base oil, is the basic building block of a lubricant. It is most often petroleum fraction, called mineral oil with composite mixture of paraffinic, aromatic, and naphthenic hydrocarbons with varying molecular weights ranging from medium to high values. Sometime vegetable oil or synthetic oil such as poly alpha-olefins, synthetic esters, silicate esters, poly alkylene glycols etc. are also used as lube oil.

The first and foremost application of the lube oils is to reduce the friction of one metal surface on another during movement in engine together with reduction of heat generation in engine by forming a physical barrier i.e., a thin layer between the moving parts in a system. Along with lubrication a lubricant performs a number of other functions. These include cooling, cleaning and suspending, protecting metal surfaces against corrosive damage, reduced variation of oil viscosity with temperature, low temperature oil flow ability, less fuel consumption, protection against wear, rust inhibition, and so on. With the improvement of technology and varying kinds of modern engines, more and additional demands for technically improved lube oil are increasing which include multifunctional performance, cost benefit along with environmental protection.Natural petroleum based lube oils are not able to satisfy all the request of modern engine. As a result, some external compounds called lubricating oil additives[2-12] are added in lube oil to improve the properties already present or to impart additional desirable properties.

The additive doped lube oil is termed as commercial lubricant. The examples of already-existing properties include pour point, viscosity, viscosity index, oxidation resistance etc. The examples of new properties include cleaning and suspending ability, anti-wear performance, corrosion control and so on. According to need and field service performance the additives are used as single chemical or mixture of two or more compounds in base oil in different concentration. Structurally most of the additives have long chain hydrocarbon unit to make them soluble in base oil.

Normally lube oil additives can be divided in three categories:

a) Surface additive: These of additives protect the metal surface from rust or wear by creating a protective film on them. Corrosion inhibitors[4], anti-wear[4,5] extreme pressure[2], friction modifier[3] 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[6,7] and foam inhibitor[8] are of this type.

c) Performance enhancing additive: Certain additives are used to introduce new performance or to enhance the existing properties of base oil. These are Viscosity Modifier (VM)[9], Pour Point Depressant (PPD)[10], detergent[11], dispersant[11], demulsifier[12] etc.

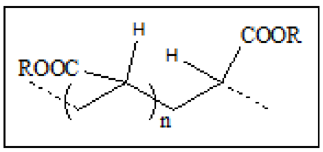
The present investigation includes the synthesis of some polymeric additives, followed by their characterization and performance evaluation as PPD, VM, and shear stability in base oils. Brief description of these additives is depicted below.

Pour point depressant: Most mineral oils contain some dissolved waxy materials and with decreasing temperature, this waxy component begins to separate as tiny crystals that interlock to form a rigid structure that traps a substantial amount of oil in small pockets in the structure and thus inhibiting oil flow. The solution becomes hazy at a certain temperature known as cloud point. If the temperature is decreased far enough, more and more wax precipitates, the crystals grow into plates, and finally the plates will grow together to form a three-dimensional network that totally immobilizes the oil. This solidification process is also referred to as gelation. The lowest temperature at which the oil becomes semi solid and loses its flow ability, is the Pour Point (PP)[13-17] of the oil. The pour point may also be defined as the lowest temperature at which oil can flow. Usually, the pour point is indicative of the presence and crystallization of wax material in oil.

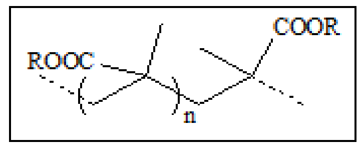
Most of the wax is removed from the base oil during refining process but some wax is still needed for achieving the proper viscosity. Extensive dewaxing also decreases the oxidation stability of base oils and increases the formation of carbon deposits. So some external ingredients are required to be added which improve the function of mineral oils efficiently at low temperatures, keeping the viscosity benefits of the wax at higher temperatures. These are the Pour Point Depressants[18-22] (PPDs) or flow improvers which are designed to lower the temperature at which wax crystals of petroleum base lubricating oil start to build up.

There is interesting mechanism of action of PPDs in base oil. It was well known that alkyl aromatic compounds coated the surface of the wax crystals and prevent further growth. Although the precise way of how PPDs operate is not absolutely clear, they all really modify the crystal morphology by various mechanisms involving nucleation, co-crystallization, and adsorption[23-25]. Light microscopy reveals that wax crystals are usually thin plates or blades. As earlier mentioned, PPDs are polymeric compounds with long hydrocarbon chain. This linear structure assists to modify the wax crystal growth by co-crystallization along with the wax species present in the oil[24]. Thus the lateral crystal growth is inhibited and the wax crystals are kept apart from each other by the PPD backbone. PPDs inhibit wax crystals from agglomeration or solidification at low temperatures. Therefore, the wax crystals are no longer able to form three-dimensional network to inhibit oil flow and thus the bulk oil remains in a liquid state.

PPDs are polymeric compounds with long chain hydrocarbon. Most common PPDs are ethylene-vinyl acetate copolymers,[26] fumerate copolymers,[27, 28] poly (acrylates),[29] poly (methacrylates),[20,30] etc.



poly(acrylate)



poly(methacrlate)

Figure 1. Structure of commonly used pour point depressants

Viscosity modifier: Viscosity Modifiers (VMs) or Viscosity Index Improvers (VIIs) are substances that improve viscosity index[31, 32] of oil by resisting the change of viscosity with temperature in lubricating oil. The viscosity index (VI) is an indicator of the change in viscosity as the temperature is changed. A high viscosity index reveals small change of viscosity with temperature and vice versa[33].

The viscosity of a lubricant is the measure of its ability to reduce friction and increases with decreasing temperature. When the temperature is low lubricant becomes too viscous and there require a large amount of energy to move, on the other hand when temperature becomes higher it becomes so thin that surfaces will come in contact and friction will increase. Many lubricant applications systems want lubricants which work at great performance levels over a wide temperature range. So, the lubricant having high VI or with least viscosity, but still minimizing friction between two moving surfaces is desired. Above all, addition of certain oil-soluble polymeric ingredients to base oil has significantly improved its viscosity index. Some of them are olefin copolymers (OCPs), poly (butenes),[34,35] poly (isobutylenes) (PIBs),[36] hydrogenated styrene isoprene copolymer (SIP), ethylene α-olefin copolymers, poly (acrylates), poly (methacrylates)[37,38] and polyalkylstyrene[39] etc.

VI improvers are long chain, high molecular weight polymers that increases the relative viscosity of oil more at high temperatures than at low temperatures. The reason of this is due to a change in the polymer's physical configuration with increasing temperature of the base oil. It is suggested that in cold oil the polymer molecules adopt a coiled structure so that their effect on viscosity is minimized. In hot oil, the polymer molecules open up in straight chain like configuration which has greater volume, and the interaction between these long molecules and the oil creates a proportionally greater thickening effect. This increase in volume of the additives causes increase of base oil viscosity which compensated the normal reduction on base oil viscosity with higher temperature.[40]

The process of polymer coil expansion is entirely reversible as coil contraction occurs with decreasing temperature.

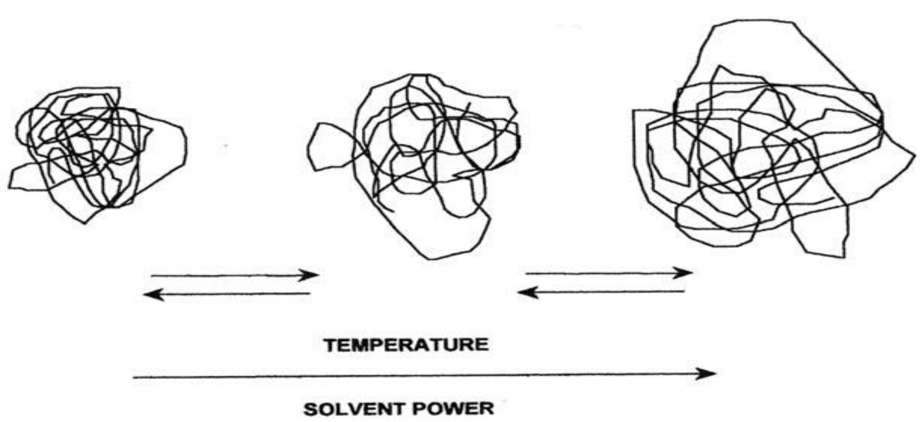


Figure 2. Expansion of viscosity modifier with temperature

As temperature increases, solubility improves, and polymer coils ultimately expand to some maximum size and in so doing provide more and more viscosity. Higher molecular weight of the VM also increases effective volume in oil solution and shows greater viscosity index.

In “poor” solvents attractive interactions force between the polymer seg-ments dominate resulting in a collapse of the polymer chains into compact polymer globules. In “good” solvents repulsive forces between polymer segments dominate resulting in an expansion of the polymer globule into a random polymer coil. Generally, as temperature increases, the solvent becomes more effective and can induce a globule -to-random coil transition.

Although people have studied and reported number of additives working either only as a VM[9,41,42] or PPD[20,43-45] additive or few more based on offering bifunctional properties like VM-PPD[46] but literature regarding multifunctional but shear stable additives are very scanty till date. With the advent of technology and development of modern engine, cost effective and eco-friendly additives providing multifunctional properties in lubricating oil are more demanding to satisfy OEM needs or consumer requests. To meet this demand attempts were made to introduce multifunctional performance in a single additive system. In the present research, some acrylate based system and also Ionic liquid blended poly acrylate systems were synthesised and their multifunctional performance were investigated. Considerably lower amount of Ionic liquid was used to ensure cost benefit.

Moreover, the concept of greener and eco-friendly technology was also incorporated by means of the green units, naturally occurring rice-bran oil, palm oil. The additive doped lubricating oils exhibited excellent multifunctional performance along with very significant biodegradability. Briefly, the thesis includes synthesis, characterization, and performance evaluation of wide variety of different polymeric additives for lube oils. The characterization of the polymers was carried out spectroscopically (by FT-IR and NMR) followed by determination of thermal stability through Thermogravimetric Analysis (TGA). Molecular weight of the polymers was determined by viscometric analysis or by gel permeation chromatographic method (GPC method). Finally performance evaluation of the additives mainly as Pour Point Depressant (PPD), Viscosity Modifier (VM) and shear stability were carried out by standard ASTM methods in different base oils. Alsobiodegradability 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. 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 (Page No 171-175).