

General Introduction of Present Investigation

From the early days of civilization, lubricants are used to assist in reducing the energy needed to slide one object against another¹. Although the use of lubricants is very old, scientific focus on lubricants and lubrication technology is relatively new. It is recorded that grease, oil, or mud have been utilized as lubricant as early as 2400 B.C. and liquid lubricant was valuable for transporting sledges in the Sumerian and Egyptian civilizations².

Lubricating oil, also known as base oil or lube oil, is the basic building unit of a lubricant. It is most often petroleum fraction, called mineral oil. It is complex mixture of paraffinic, aromatic, and naphthenic hydrocarbons with varying molecular weights ranging from medium to high values. Vegetable oils or synthetic oils such as polyalpha-olefins, synthetic esters, silicate esters, polyalkylene glycols and many others are sometimes used as base oils. The quality of base oils is determined by their olefinic, nitrogenated, aromatic, and sulfured compound contents. During the Hydro Treatment (HDT) process, the operational conditions of low or medium severity are maintained so that aromatic distribution in the oil is not seriously affected and sulfur compounds are not completely removed.

In field application, lube oil forms a physical barrier i.e., a thin layer between the moving parts in a system, thus reducing friction and surface fatigue, together with reduced heat generation in engine. Along with friction reduction and heat transfer, lube oil has to perform a number of other functions in an engine e.g. reduced variation of oil viscosity with temperature, low temperature oil flow ability, less fuel consumption, corrosion prevention, protection against wear, rust inhibition, and so on. The technically developed modern engines need technically improved lube oil with improved efficiency to show multifunctional performance and cost effectiveness along with environmental protection. Natural petroleum based lube oils are not able to meet all the demands of modern engines.

As a result, some external compounds called lubricating oil additives³⁻¹³ are added in lube oil to improve the properties already present or to impart additional desirable properties and the additive doped lube oil is termed as lubricant. Generally lubricants are based on one type of base oil though mixtures of the base oils are also used plus a variety of additives to meet desirable performance necessary for efficient operation and prolonged engine life. No single additive can meet Original Equipment Manufacturer (OEM) needs or consumer requirements. Thus, several additives are needed to deliver the performance required which changes with engine design, operating conditions, legislation, source of supply, and processing methods of the base oil. Several additives of different chemistry are used, at concentrations from 0.005 % to more than 10 % by weight of some lubricant. Without the additives the oil would become contaminated, break down, leak out, or not protect engine parts properly at all operating temperatures and subsequently frequent oil change is required. So oil additives are vital for the proper lubrication and prolonged use of motor oil in modern internal combustion engines.

Generally lube oil additives 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 pressure³, friction modifier⁴, corrosion inhibitors⁵, anti wear^{5,6} etc. are examples of this kind.
- b) **Lubricant protective additive:** These additives protect the additives in lube oil from oxidation, high temperature breakage etc. Antioxidant^{7,8} and foam inhibitor⁹ are of this type.
- c) **Performance enhancing additive:** Some additives are used to introduce new performance or to enhance the existing properties of base oil. These are Viscosity Modifier (VM)¹⁰, Pour Point Depressant (PPD)¹¹, detergent¹², dispersant¹², demulsifier¹³ etc.

The present investigation comprises the synthesis of some polymeric additives, followed by their characterization (by spectral, thermogravimetric and viscometric analysis) and performance evaluation as PPD and VM in base oils. Brief description of these additives is depicted below.

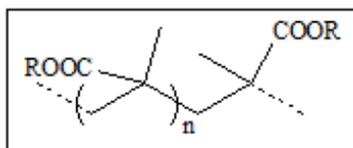
Pour point depressant: The paraffinic mineral base oils contain small amounts of waxy materials. With decreasing temperature some of the waxy components of the oil tend to separate as tiny crystals, trapping a substantial amount of oil, and thus inhibiting oil flow. The solution becomes hazy at a definite 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)¹⁴⁻¹⁸ of the oil. The pour point may also be defined as the lowest temperature at which the oil maintain its intended fluidity when cooled under defined conditions. Generally, the pour point is indicative of the amount of wax in oil and a high pour point means high paraffin content in the oil.

During refining process, most of the wax is removed from the base oil but some wax is still desirable 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 substances are needed to be added which allows mineral oils to function efficiently at low temperatures, keeping the viscosity benefits of the wax at higher temperatures. These are the **Pour Point Depressants**¹⁹⁻²³ (PPDs) or flow improvers which are designed to lower the temperature at which wax crystals of petroleum base lubricating oil start to build up. The flow characteristics of lubricants without PPDs can be adversely affected, causing a negative impact on engine performance.

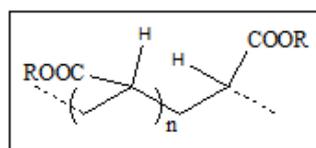
Previously used PPDs are predominantly oligomers with molecular weights of 1,000 to 10,000 or polymers having molecular weights greater than 10,000. The earlier PPDs were either alkyl aromatic polymers or comb polymers. Comb polymers characteristically have long alkyl chains attached to the backbone of the polymer, with the alkyl groups of different carbon chain lengths.

The mechanism of action of PPDs has been the subject of much interest. Early indications were that alkyl aromatic compounds function by coating the surface of the wax crystals and preventing further growth. Although the exact way of how PPDs operate is not absolutely clear, they all basically modify the crystal morphology by different mechanisms involving nucleation, co-crystallization, and adsorption²⁴⁻²⁶. Light microscopy suggests that wax crystals are typically thin plates or blades. As previously mentioned, PPDs are polymeric compounds with long hydrocarbon chain. This structural linearity assists to modify the wax crystal growth by co-crystallization along with the wax species present in the oil²⁵. Thus they inhibit lateral crystal growth and the wax crystals are kept apart from each other by the PPD backbone. PPDs prevent wax crystals from agglomerating or solidifying at reduced temperatures. Thus the wax crystals are no longer able to form three-dimensional structures to inhibit flow and the bulk oil remains in a liquid state.

Most common PPDs are fumarate copolymers²⁷, ethylene-vinyl acetate copolymers^{28,29}, poly (methacrylates)^{21,30}, poly (acrylates)³¹ etc. They are used in almost all lubricant types including crankcase engine oils, automatic and power transmission fluids, automotive gear oils, tractor fluids, hydraulic fluids, and circulating oils.



Poly (methacrylate)

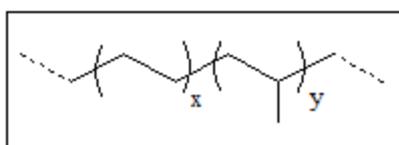


Poly (acrylate)

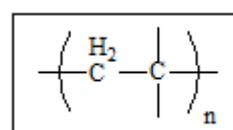
Figure 1. Structure of commonly used pour point depressants

Viscosity modifier: Viscosity Modifiers (VMs), previously known as **Viscosity Index Improvers (VIIs)** are substances that improve viscosity index^{32,33} of oil. **Viscosity Index (VI)** is an arbitrary measure of viscosity changes with relation to temperature in lubricating oil. A high viscosity index indicates small change of viscosity with temperature and vice versa³⁴.

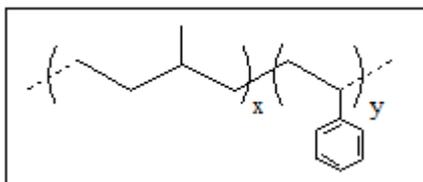
The viscosity of a lubricant is generally its ability to reduce friction and decreases with increasing temperature. At lower temperature if the lubricant becomes too viscous, it will require a large amount of energy to move and if it becomes too thin at higher temperature, the surfaces will come in contact and friction will increase. Many lubricant applications require lubricants to work at high performance levels over a wide temperature range. So, the lubricant with high VI or with least viscosity, but still keeping two moving surfaces apart is desired. In particular, addition of certain oil-soluble polymeric materials to base oil has greatly improved its viscosity index. Some of them which are in use today are olefin copolymers (OCPs), poly (isobutylenes) (PIBs)³⁵, hydrogenated styrene isoprene copolymer (SIP), ethylene α -olefin copolymers, poly (acrylates), polybutadiene rubber (PBR), poly (butenes)^{36,37}, poly (methacrylates)^{38,39} and polyalkylstyrene⁴⁰ etc.



Ethylene-propylene copolymer (OCP)



Poly (isobutylene) (PIB)



Hydrogenated styrene-isoprene copolymer (SIP)

Figure 2. Structure of commonly used viscosity modifiers

The well accepted mechanism of how polymers improve VI originates from a paper by Selby in 1958⁴¹ which is lacking in any physical data supporting the proposed mechanism. Later, the work of Flory stated that the radius of gyration, R_g , of polymer molecules depends on the interactions between polymer chain segments and solvent molecules⁴². In the “poor” solvents, attractive interactions act between the polymer segments, resulting in a collapse of the polymer chains into compact polymer globules, while expansion of the globule into a random coil occurs in “good” solvents where repulsive forces act between those polymer segments⁴³. At higher temperature while the viscosity of the lube oil gets decreased, the polymer molecules thicken the oil by changing shape from tight coil or globule to expanded random coil due to increased polymer-solvent interaction and thus offset the viscosity reduction⁴⁴⁻⁵⁰. This thickening effect is more effective at higher temperatures than at lower temperatures as with increasing temperature, the solvent becomes more effective and can induce a globule-to-random coil transition. Again, increasing polymer concentration increases total volume of polymer globules in the solution which induces a higher viscosity index compared to a lower one.

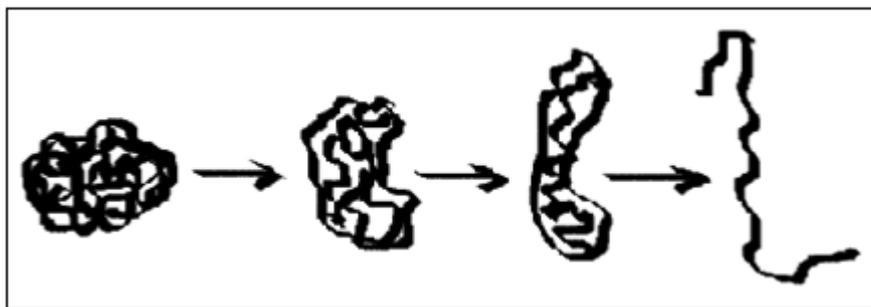


Figure 3. Expansion of viscosity modifier with temperature

In a very recent communication Michael J. Covitch et al. presented a detailed report⁴³, the aim of which is to develop an improved model that is consistent with experimental data by linking the rheological properties of a fluid to the polymer structures in solution. The experiment involves measurement of polymer coil dimensions of VMs by both intrinsic viscosity and Small Angle Neutron Scattering (SANS) in order to critically assess the generally accepted mechanism of VI improvement. The observed results indicated that coil size expansion with temperature is not required mechanism to achieve significant elevation of viscosity index but the polymers which expand with temperature have higher VI contributions than those that do not.

The additives reported till now work either as PPD^{21,51-53} or VM^{10,45,54} or studies regarding multifunctional additives based on both these properties are very scanty. With the advent of technology, cost effective and eco-friendly multifunctional lubricating oil additives are more demanding to meet OEM needs or consumer requirements. In the present investigation, some acrylate systems were synthesised and evaluated for multifunctional additive performance. In addition, the concept of greener technology was also incorporated by using the green units, naturally occurring α -pinene and sunflower oil. 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 some 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. Finally performance evaluation of the additives mainly as Pour Point Depressant (PPD) and Viscosity Modifier (VM), were evaluated by standard methods in different base oils. Biodegradability study was performed for some of the polymeric systems 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 of present investigation (Page No. 177-182).