General introduction of the present investigation

The development of engine and transmission technology is not possible without the development of chemistry of lubricant additives. The lubricant companies are working with the partnership of Oil Company and the automotive industries to enhance longevity and performances of engine and the drive line system through lubricant design.[1]

Lubricating oil, also called base oil, is the basic building block of a lubricant. They are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from C_{20}-C_{70} (boiling range 622-673K).[2] The main role of the base oil is to lubricate the engine and it is a carrier of additives. They are less volatile and with high value of viscosity index. The proportions of different hydrocarbon components determine the characteristics of the base oils. The performance of lubricant base oils is governed by their rheological properties such as low temperature fluidity, high viscosity and viscosity temperature relationship. For example, to provide an effective performance at low temperature as well as at high temperature, an engine lubricant should have good low temperature fluidity and small variation of viscosity with rise in temperature.[3]

Until the 1920s the engine oil contained no additives, containing only base oil. Due to increasing economic pressures and consumer demands, the internal combustion engines were becoming more innovatory. The base oil can’t satisfy all the requirements of modern engines. To improve the performance of the base oil, different kinds of additives are blended. Additives are the polymeric or non polymeric synthetic compounds. The additives blended base oils are called lubricants. The lubricants are more compatible to the new technology.[4] They not only improve the performance of the base stock that already present in it but also add some new properties.[5] The main role of additives are to

a) enhance the lifetime of machine

b) enhance fuel economy

c) induce better performance

d) help in achieving green technology

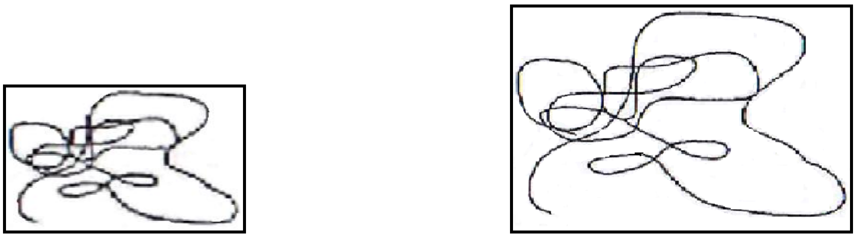
e) reduce pollution.

Thus research and development of additive chemistry for lube oil definitely improves the pursuit of original equipment manufacturer (OEM) in the technology sector. The combination and quantities of different additives are determined by the lubricant type (engine oils, gear oils, hydraulic oils, compressor oils etc) and depending on operating conditions (temperature, loads, environment, parts of machine etc). The addition of amount of additives may reach up to 30% (w/w) to the lube oil.[6]

Types of lube oil additives: Different types of lube oil additives are

i) Viscosity index improver (VII) or Viscosity modifier (VM) ii) Pour point depressant (PPD) iii) Antiwear additive (AW) iv) Friction modifier (FM) v) Antioxidant (AO) vi) Detergent vii) Dispersant viii) Extreme pressure additive (EP) ix) Rust and corrosion inhibitor x) Anti-foam agent.

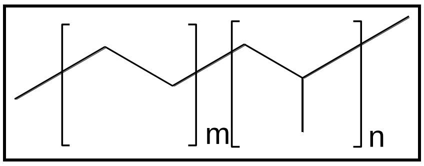
Viscosity Index Improver: The degree of susceptibility of viscosity of a fluid with rise in temperature variations is quantitatively expressed by an empirical term known as viscosity index (VI). Viscosity index improvers (VII), also known as viscosity modifiers (VM) are additives that resist the change of viscosity of oil with change in temperature.[7] They cause a minimum amount of increase in engine oil viscosity at low temperature, but considerable amount of increase at high temperature. A higher VI value signifies a lesser effect of temperature on viscosity. Viscosity index improvers keep the viscosity at acceptable level which provides stable oil film even at increased temperature. Acrylate based polymers are widely used as VII in lubricants. It is believed that in cold oil the polymer molecule adopt a coiled form but in hot oil the long chain polymer molecule swells up and interaction between the polymer molecule and the oil produces proportionally greater thickening effect which offsets the normal reduction of viscosity with rise in temperature.[8]



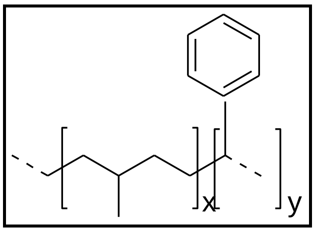
Polymer in lube oil at low temperature Polymer in lube oil at high temperature

Figure 1 Effect of temperature on polymeric additive in lube oil.

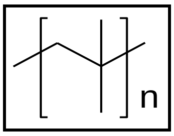
Higher molecular weight polymers are widely used as VII for multigrade lubricants. Olefin copolymers, hydrogenated styrene-diene copolymers, maleic anhydride based copolymers, polyisobutylene, polyalkylmethacrylates, vegetables oil based polymers etc. are widely used as VII for multigrade lubricants.



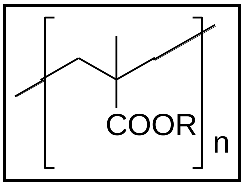
Ethylene-propylene copolymer



Hydrogenated styrene-isoprene copolymer



Polyisobutylene



Polyalkylmethacrylate

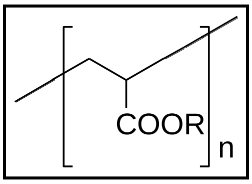
Figure 2 Structure of some commonly used viscosity index improver

Pour point depressant: Pour point is the lowest temperature at which the flow of fluids is stopped. Lube oil contains some paraffinic wax (generally 5% - 20%). The complete removal of paraffinic wax from lube oil is difficult and expensive; pour point depressants provide an economical means of facilitating the flow property of oil in an engine at low temperature.[9, 10] At low temperature, the paraffinic wax crystallizes to form a rigid structure that traps the oil molecule and hinders the flow capability. Pour point depressants, otherwise known as lube oil flow improvers (LOFI), are those additives that improve the low temperature fluidity of the fluid. The pour point depressants function by inhibiting the formation of a wax crystal structure that would prevent the oil flow at low temperatures.[11, 12] The polymeric additives which are used as PPD should have some pendant alkyl groups and there should be an appropriate distances among the pendant groups.[13, 14] Moreover, there should be a suitable monomer-monomer ratio in the copolymers which are used as PPD.[15]

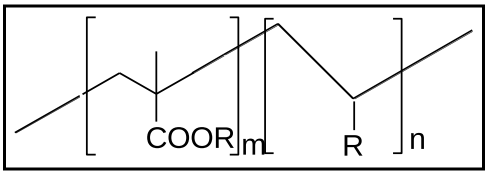
Wax crystal — Polymeric additives — controlled growth of wax

Figure 3 Schematic representation of the action mechanism of additives on wax crystal

Polyalkylacrylates, copolymers of polyalkyl methacrylate,[16] maleic anhydride based polymeric additives, vinyl acetate based polymeric additives[17] and recently polymers of vegetable oils are widely used as PPD in lubricants.[18]



Polyalkylacrylate



Copolymer of alkylmethacrylate with α- olefin

Figure 4 Structure of some commonly used pour point depressant

Antiwear additive: The antiwear additives prevent the direct metal to metal contact of the two moving parts of an engine when the oil film is broken down. The antiwear additives enhance the life of the machine. The mechanism action of anti-wear additives is that strong adsorption or chemisorptions takes place between the AW additives and the metal surface and generates a film, which may slide over the friction surface. In case of chemisorptions sometimes electron transfer occurs between additive molecule and metal surface.[19]

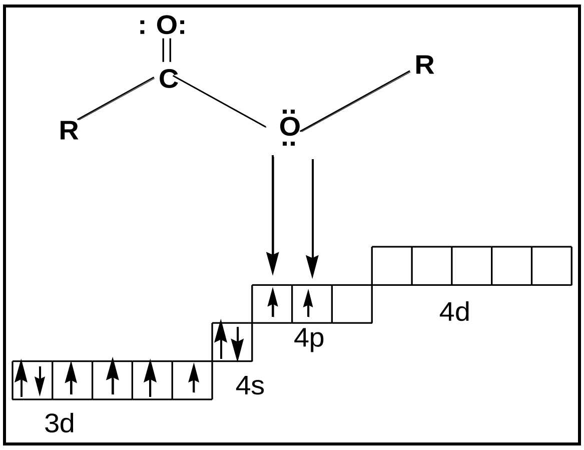
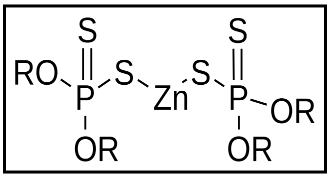
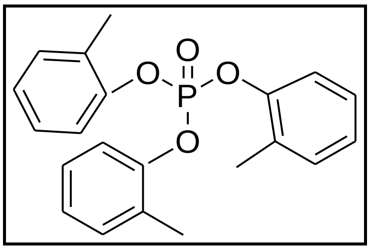


Figure 5 Schematic representation of donor accepter bond between AW additive and metal (Fe) surface

Organosulfur, organophosphorus compounds are widely used AW and extreme pressure additives. Zinc dialkyl dithio phosphate (ZDDP) is the most widely used AW additive in formulated engine oils.[20] It also acts as an antioxidant and corrosion inhibitor. Tricresyl Phosphate (TCP) is used as AW and EP additive in turbine engine lubricants, and also in some crankcase oils and hydraulic fluids. Recently liquid crystals, ionic liquid,[21] nanoparticles [22] and environmentally benign vegetable oils based additives[23] are used as AW for lubricating oils.



Zinc dialkyldithiophosphate



Tricresyl phosphate

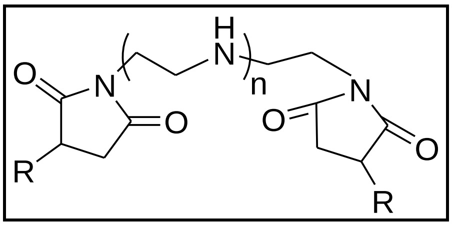
Figure 6 Structure of some commonly used antiwear additives

Friction modifier: The additive which reduces the coefficient of friction and hence less fuel consumption is called friction modifiers. Most of FM consists of molecular platelets which may easily slide over each other. The mechanism action of FM is that they generate durable low resistance lubricant films through adsorption on surfaces and association with the oil. Long chain fatty acid and its derivatives, graphite, molybdenum, boron nitride (BN), Tungsten disulphide (WS_2), polytetrafluoroethylene (PTFE) etc. are the lubricants used as FM.

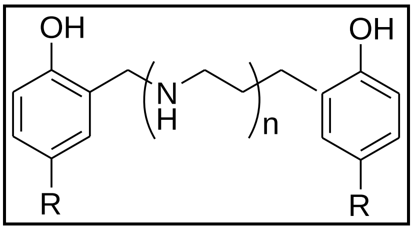
Antioxidant additive: Lubricating oil reacts with oxygen of air or heat forming some organic fatty acids, fatty alcohols, fatty aldehydes and ketones, fatty esters, peroxides etc. The Fe/Cu metal present in internal engine part supports the oxidation process by acting as a catalyst. All oxidized products are solid asphaltic materials. The oxidation products are responsible for the increase of oil viscosity, formation of sludge and varnish, corrosion of internal engine part and reduced fuel economy. For this reason, addition of antioxidants to lubricating oil is necessary to prevent the formation of these products. Alkyl sulphides, aromatic sulphides, aromatic amines, hindered phenols, zinc dithiophosphate (ZDP) etc. are the compounds widely used as antioxidants in lubricating oil. The antioxidant like hindered phenols and aromatics amines transfer hydrogen atom from –OH and $–NH_2$ group respectively that react with alkyl radicals or alkyl alkoxy radicals that was generated during the oxidation of oil. As a result, alkyl radical and alkyl alkoxy radical convert into stable hydrocarbon and alkyl hydro peroxide respectively. After transferring the H-atom, the phenols or amines convert into quinines or quine imines that don’t maintain the radical chain mechanism.

Detergent and dispersant additives: Detergents are the additives which neutralize strong acids present in the lubricant and remove the neutralization products from the metal surface of the engine. The strong acids are generated as a result of combustion process in the internal combustion engine.[24] Detergents are the phenolates, sulphonates or phosphates of alkaline or alkaline earth metals such as Ca, Mg, Na or Ba etc.

The additives which keep the foreign particles present in a lubricant in a finely divided and uniformly dispersed throughout the oil are called dispersant additives.[25] The foreign particles are generally sludge and varnish, dirt, products of oxidation, water etc. Long chain polyisobutylene succinimides,[26] Mannich bases and phosphosulphurized Mannich bases of hindered phenols,[27] amidation products of maleic anhydride and alpha olefin copolymer[28] etc. are widely used as dispersants in lubricants.



Succinimide based dispersant



Mannich base type dispersant

Figure 7 Structure of some commonly used dispersant additives

A dispersant molecule consists of a hydrocarbon group, nitrogen or oxygen based polar group and a connecting group, shown in the figure......

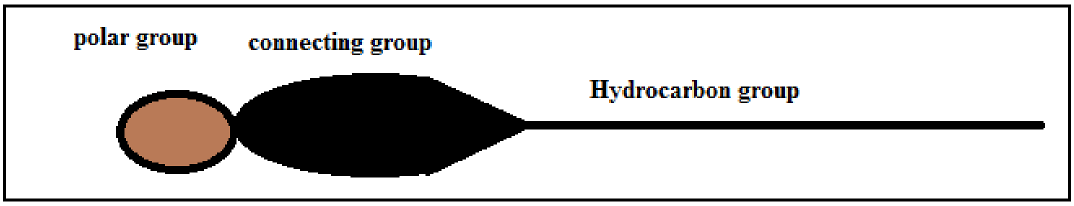


Figure 8 Graphical representation of a dispersant molecule

Dispersants prevents in agglomeration by associating with resigns and soot particles. The associated dispersant molecule is incompetent to unite due to steric factors or electrostatic factors. The polar group of the dispersant molecule is associated with the polar particles and the non polar group (hydrocarbon group) keeps such particles suspended in the bulk lubricant.[29]

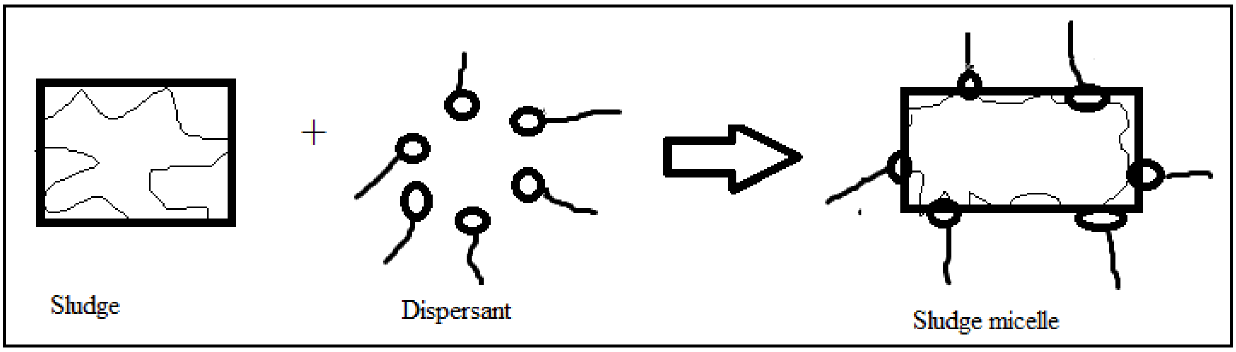


Figure 9 Action mechanism of dispersant

Although many researchers have studied and reported number of additives or polymeric additives functioning either only as a VM[30] or PPD[31] or AW[32] additive or some works based on bifunctional properties like VM-PPD[33] or VM-AW[34], antioxidants - detergents /dispersants[35] etc, but the research based on polymeric additives having multifunctional properties are very scanty till date. With the development of engine technology, the modern engines are demanding high quality, cost effective and environmentally benign additives[36-38] having multifunctional performance. Keeping these views in mind, the author have made an effort to achieve some multifunctional additives in a single additive system to meet the above demands. Some methacrylate and maleic anhydride based polymeric additives were synthesised and multifunctional additive performance were also evaluated. Keeping the concept of greener technology in mind, the present investigation also comprises the synthesis and performance evaluation of vegetable oil based multifunctional additives. Vegetable oils used in this study are sunflower oil and castor oil. The additive doped lube oils manifested excellent multifunctional additive performance along with very significant biodegradability.

In brief, the thesis comprises synthesis, characterization and performance evaluation of a numbers of different additives for lubricating oils. The characterization was carried out by spectroscopic method (FT-IR and NMR). The thermal stability was determined by thermo gravimetric analysis (TGA) method. Molecular weight of the polymers was determined by gel permeation chromatographic method (GPC method) and in some cases by viscometric method. Finally performances of the additives mainly as viscosity index improver (VII) or viscosity modifier (VM), pour point depressant (PPD), in some cases antiwear (AW), antioxidant and detergent/dispersant were evaluated by standard ASTM methods in different base oils. Degradation stability (in terms of shear stability) of some of the prepared additives were also determined and reported. Biodegradability study was carried out by disc diffusion method and soil burial test method using different fungal pathogens according to ISO 846:1997 rules. Photo micrographic image and powder XRD of some of the PPD were also carried out in base oil to study the mechanism action of pour point. The outcome of our present investigations has some potential additives for lubricating oil which will be dealt with for commercial application and will be the taken up by our group in near future. In addition, the investigation has also contributed to the lube oil additive chemistry and will definitely help to grow interest in research among the young scientists in the field of additive chemistry for lubricating oil.

References

References are given in bibliography section under general introduction of present investigation (Page No. 175 - 178).