PART-I

Acrylate and methacrylate based polymers as multifunctional lube oil additives

Chapter-I

Background of the present investigation

The lube oil or base oil is the basic building unit of a lubricant and is generally produced by refining crude oils. Crude oil consists mostly of carbon (81-85%) and hydrogen (10-12%) and has a complex mixture of hydrocarbon like paraffins, naphthenes, aromatic and gaseous hydrocarbons. Crude oil also contains small amount of non hydrocarbons like sulphur, nitrogen and oxygen compounds. Depending on predominance of hydrocarbons, petroleum is classified as paraffin base, intermediate base or naphthenic base.

Although the primary function of a base oil is to reduce friction and wear between surfaces which are in contact with each other, they are also associated with a large number of secondary functions such as cooling, cleaning, suspending the impurities, maintaining low temperature flow ability etc. However, in most of the cases the base oils do not meet the current technical requirements of the original equipment manufacturers (OEM) because of their limited performance. The base oils are, therefore, blended with different additives in an expectation to improve their lubrication properties.[1] The additives cover a wide range of chemicals starting from simple molecules (organic or inorganic) to large polymeric compounds. They are selected according to the property to be introduced in the base oil and can be blended as single compound or even as a mixture of compounds to formulate the finished lubricants. Thus, the formulation of a high-performance, user friendly and cost effective lubricant largely depends on the quality of the base oil, the selection of suitable additives and their proportions. The selection of the additives, thus, requires skill and experience which will exploit the various dimensions of synergism and will relieve the known weaknesses of the base oil. The base oils with distinct properties hence acts as a carrier of additives. According to the specific functions an additive can perform, they can be classified into the following types.

Figure 6. Different types of lube oil additives

The success of a lubricant in delivering the highest level of performance depends upon understanding the interactions of the additives with the base oil and matching those to the requirements of equipments and the operating conditions to which they are exposed. Without the additives, the oil may not shield the engine properly at all operating conditions and this might lead to contamination, break down, overheating and permanent damage to the engine.

Additives have to perform a number of functions, but usually only one additive cannot satisfy all the requirements of the advanced engines. Thus, proper mixtures of different types of additives are mixed to the base oil. But, keeping in mind the cost effectiveness and the hazardous nature of the chemicals used in this field, the demand for multifunctional additive is on the rise.[2-7] Multifunctional additives not only increase the life span of lubricating oils but can also increase the lifetime of engine at a cheaper cost. Therefore, research all over the world is increasingly focussed toward producing

multifunctional additives.[8-10] Acknowledging this fact, the present study comprises the incorporation of two major additives (VII and PPD) in single additive system. Also, the numerous studies on high molecular weight polymeric compounds used as lube oil additives and the experienced gathered from that has serve as a opportunity in the development of multifunctional polymeric additives that have both VII and PPD properties.

Since our present investigation is on "acrylate and methacrylate based polymers as multifunctional lube oil additives", it will be very relevant to include a brief review on VII and PPD additives of lubricating oil.

As already discussed in the general introduction section, viscosity is a very important property of a lubricant and is a measure of a fluid's resistance to flow. At higher temperatures, the oil tends to thin out resulting in reduction in viscosity and this affect its flow ability. The parameter chosen to express the change in the viscous nature of the lube oil with temperature is called viscosity index (VI). A higher VI indicates a small change in viscosity with rise in temperature and vice-versa.[11,12] Viscosity index improvers (VIIs) or viscosity modifiers (VMs) are additives that are added to lubricating oils to make them behave as ideal lubricant which possess almost the same viscosity at all temperatures.[13-18] Long chain high molecular weight polymeric compounds are generally used as VIIs and their efficiency depends on the type and concentration of the additive.[19] They generally work by changing their arrangement from tight coils to an open configuration with increasing temperature. This open configuration results in greater association with the base oil and thus a greater thickening and which offsets the normal reduction of viscosity with increasing temperature.[20-23]

Again, base oils contain substantial amounts of oil waxes called paraffins in them. Paraffins are complex mixtures of hydrocarbons containing linear chain predominantly

of 20 to 40 carbon atoms and alkanes with branched and cyclic chains. As the temperature decreases, the paraffin crystals grow generating a crystalline net which entraps the molecules of liquid hydrocarbon until the oil cannot flow.[24-26] The temperature at which this happens is called the pour point (PP). Pour point depressants (PPDs) are designed to prevent the agglomeration of wax particle present in lubricating oils.[27-30] If lube oils are not appropriately blended with PPDs, the flow characteristic of lube oils are highly affected which in turn affect the engine performances. The mechanism of function of PPD also grabbed much interest. It was initially believed that the PPD additives coat the paraffinic wax crystals preventing their further growth. More recently, it is believed that PPD functions by co-crystallization, nucleation or adsorption and disrupting the formation of three dimensional wax crystals network.[31-34] An efficient PPD should be a linear polymer with pendant hydrocarbon chain groups and also with an appropriate distance between the pendant chains in the polymeric backbone. Suitable ratios between the co-monomers, nature (amorphous or crystalline) of the additive and suitable molar mass are also the determining factors for an additive to work as effective PPD.[35-38]

The alkylacrylate and alkylmethacrylate are one of the most popular VII and PPD for lube oils. Due to the presence of ester linkage, they are more polar than ethylene/propylene or styrene polymers and the presence of long chain alkyl group in them imparts solubility into the lube oil. Methacrylate monomers with different alkyl chains can be copolymerized in an identical copolymerization reactivity ratio and in a statistically random distribution irrespective of the size of the alkyl groups. Various studies of previous researchers in accordance with the present line of investigation regarding VII and PPD are being discussed in the following paragraphs.

In the year 1937, Rohm and Haas patented the first polymeric PPD, poly alkyl methacrylates (PAMAs) based on waxy alkyl groups. Few years later, Ruehrwein reported the action of n-alkyl poly methacrylate as PPD in the series of methacrylate containing 12 to 18 carbon chains. It was reported that the longer alkyl chain polymers were effective as PPD in case of high temperature pour oils, while the shorter alkyl chain polymers were efficient on lower temperature pour oils.[39] Gavlin *et al.* analysed some acrylates and methacrylates for their PPD properties. Dodecyl methacrylate was chosen by the authors for their work and it was their first acrylic polymer to have excellent PPD properties.[40] A number of copolymers based on alkyl fumarate and vinyl acetate were synthesised by Borthakur *et al.* and their effectiveness as PPD was tested on Indian crude oils.[41] El-Gamel *et al.* in the year 1997 reported the synthesis of α-olefin-alkyl methacrylate as PPD for waxy residue fuel. Their study suggested that the polymer containing alkyl group consisting of 21 carbon chain are superior as PPD.[42]

Jian *et al.* prepared some esterified copolymers made from different fractions of maleic anhydride and α-olefin and termed them as EsMAOC polymers. The PPD performance of the polymers was tested in crude oil and heavy diesel oil.[28] The same group reported the synthesis of MOVAS copolymer obtained from α- olefin, maleic anhydride and a mixture of vinyl acetate and styrene and evaluated the additive for their PPD performance.[43] The group also prepared a viscous semi solid MOAS copolymer from maleic anhydride, acrylic alkyl ester, styrene and mixed α-olefins (the average carbon number is 15) and analysed the synthesised polymer for their PP and cold filter plugging point (CFPP) values in diesel fuel.[44]

Abdel-Azim *et al.* in the year 2006 reported additives based on different esters of acrylic acid and different ratios of styrene to be used as PPD. They reported that the effectiveness of the prepared additives as PPD decreases by increasing the styrene

content in the feed.[45] Khidr, in the year 2007 prepared four copolymers made from 1-octene or 1-tetradecene and maleic anhydride and esterified them with dodecyl or NAFOL 1822B alcohol. The effectiveness of the copolymers as PPD was tested for crude oil and it was found that the alkyl chains of the copolymers are a crucial factor for a proper interaction of the additives with the crude oil.[46] In 2008, Farag prepared different copolymers by varying the molar concentration of cinnamoyloxy ethyl methacrylate and octadecyl acrylate and the PPD performance and rheological characteristics were studied using different concentrations of the prepared additives for two different waxy crude oils.[47]

El-Ghazawy *et al.,* in the year 2010 reported a novel PPD for waxy crude oil based on alkyl acrylate terpolymers.[48] In another work, Khidr reported the preparation of some copolymeric and terpolymeric additives of maleic anhydride and alkyl acrylates of different chain length. The polymers were tested for both PPD and wax dispersants for paraffin gas oils and satisfactory results were obtained for the additives.[49] Jung *et al.* in the year 2011, synthesized six terpolymers and twelve copolymers based on different methacrylates to be used as flow improver in lube oil. They reported that the additives made from dodecyl methacrylate, hexadecyl methacrylate and methyl methacrylate at a molar ratio of 3.5:3.5:3 exhibited the best performance as PPD.[50] In the year 2014, polymeric additives based on decyl acrylate and styrene were synthesized by Ghosh *et al.* and they found some excellent PPD results with the polymers.[51]

The effectiveness of the polymers like polyvinyl palmitate, polyvinyl caprylate and copolymers of vinyl palmitate with vinyl acetate as VII were analysed by Port *et al.* and found that the additives are efficient viscosity modifiers for lubricating oils.[52] In an experiment of Yorulmaz, the effect of degree of alkylation, the molecular weight and the size of the alkyl groups of different alkylated polystyrenes were analysed for viscosity

index improving performance.[53] Coutinho *et al.* synthesized copolymers based on ethylene-propylene and hydrogenated styrene-diene and carried out a comparative study between them considering their application as viscosity index improvers in multigrade engine oils.[54] Copolymers made of α-olefins (ethylene and propylene) were prepared by Reza *et al.* and were found to be a good VII at low concentration in motor oil formulation.[55]

Nassar *et al.* made a comparative study of some polymeric additives prepared by copolymerization of different moles of styrene with different acrylates (decyl, 1-dodecyl, 1-tetradecyl, and hexadecyl) as VIIs. The viscosity modification properties of the additives were found to increase with increasing molecular weight of the prepared copolymers.[56] Jukic *et al.* reported dodecyl methacrylate, octadecyl methacrylate and styrene based terpolymers as VII for lubricating oil. The amount of styrene in the additive was restricted to 25% by weight. The group reported that the viscosity index increased with increasing molar mass of the additive but opposite effect was obtained by increasing the styrene percentage.[57]

Additives made of dialkyl maleates with two different monomers (vinyl acetate and styrene) were synthesized by N. S. Ahmed *et al.* and their efficiency as VII (by improving the viscosity index) was studied in the base oil. The viscosity index was found to increases with increasing the concentration of the polymers in base oil and also with increasing alkyl chain length and molecular weight of the additives.[58] In 2012, Mohammed *et al.* reported additive for Iraqi lubricating oils based on poly methylmethacrylate and evaluation their performance was viscosity modifier.[59]

There are also some examples where acrylates and methacrylates are found to act as both VIIs and PPDs.

Ahmed *et al.* prepared some additives through polymerisation of vinyl acetate and maleic anhydride with different acrylates and studied the effect of concentration, molecular weight and alkyl chain length on the viscosity index and pour point values of the additives.[60] In a similar work on Mexican crude oils, different additives were synthesized from vinyl acetate, *n*-butyl acrylate and styrene. The additives were evaluated for PPD efficiency and VM tendency with satisfactory results.[61] Ghosh *et al.* reported copolymers of styrene and decyl acrylate and their compatibility as PPD and VM.[62] In other work, polymers of myristyl acrylate were synthesized by two different methods viz. thermal method and microwave assisted method and their potential to act as PPD and VII were evaluated and compared.[63]

There also has been a significant amount patent activity concerning the acrylate, methacrylate and olefinic compositions as pour point depressants and viscosity modifiers. Some of them are being presented in a selective manner, in the following paragraphs.

The U. S. Patent No. 2655479 A of Munday *et al.* reports the use of equal proportions of a copolymer of decyl acrylate and an acrylic acid ester of a mixture of alcohols derived from coconut oil to improve the PPD property. U. S. Patent No. 3598736 A describes the addition of oil soluble copolymers (containing 10 to 20 carbon atoms) of polymethacrylates to lubricating oils to improve the pour point property. A similar disclosure is also reported in U. S. Patent No. 3679644 A. The U. S. Patent No. 3598737 A reported a lubricant compositions consisting of methacrylic acid, acrylic acid and mixtures thereof which are said to improve various characteristics including pour point. The PPD ability of the group consisting of copolymers of alkyl methacrylates, alkyl acrylates and nitrogen containing esters of the acrylic acid series has been disclosed by U. S. Patent No. 3772196 A.

The U.S. Patent No. 3897353 described lubricating oil composition consisting n-alkyl methacrylate containing 12 to 18 carbon atoms as a PPD while the use of alkyl acrylate or alkyl methacrylate made from monomers with 8 to 22 carbon atoms has been disclosed by U.S. Patent No. 4073738. The use of copolymers of alkyl methacrylates containing 16 to 30 carbon atoms and with an average molecular weight ranging from 50,000 to 500,000 as PPD in petroleum oil has been reported by U. S. Patent No. 4867894 A. The use of ester of unsaturated carboxylic acid as PPD for lube oil selected from the group consisting of acrylic and methacrylic acid has been described in U. S. Patent No. 4906702 A. The preparation and evaluation of acrylate copolymers as PPD in lube oils has been reported by U. S. Patent No. 5834408 A.

The Patent No. 5955405 describes some copolymers containing 5-10 wt % of C_{16}-C_{30} alkyl methacrylate, 5-15 wt % of butyl methacrylate and 70-90 wt % of C_{10}-C_{15} alkyl methacrylate as excellent low temperature performance enhancer in lubricating oils. The use of a mixture of low molecular weight and selected high molecular weight alkyl methacrylate made of 16-24 carbon containing alcohols has been disclosed by U. S. Patent No. 6458749 B2. The patent describes effective low temperature fluid properties for a broad range of base oils. The use of copolymer as PPD prepared by polymerization of three α-olefin monomers (decene, tetradecene and hexadecane) with molecular weight ranging from 150,000 to 450,000 has been described in Patent No. CA 2059825 C. The Patent No. EP 0140274 discloses the use of additives for lubricating oil containing n-paraffin based poly alkylmethacrylate and acrylate. Similarly, Patent No. EP 0498549 B1 claims the preparation of a PPD terpolymer wherein the average alkyl side chain length is 10.5 to 12.0 and made from 10, 14 and 16 carbon atoms. The U. S. Patent No. 4514314 reported the application of alkyl ester copolymers as a PPD for

lubricating oils. These copolymers have a number average molecular weight optimally from 2,000 to 8,000 and preferably between 2,000 to 15,000.

The U. S. Patent No. 3607749 claimed the use of poly alkyl methacrylates preferably of molecular weight above 100,000 and more preferably above 350,000 as VIIs while the use of a lubricant composition with molecular weight in the range of about 100,000 to about 750,000 and containing about 0.60 to about 1.75 percent of an oil soluble poly methacrylate has been disclosed by U. S. Patent No. 4203854 A. The U. S. Patent No. WO2012076676 A1 disclosed a VII comprising poly alkyl methacrylate additive containing 10 to 15 carbon atoms in the alkyl residue. The use of olefinic copolymers, such as copolymers of ethylene, propylene, diolefin etc for viscosity modification of lubricating oils is disclosed in U. S. Patent No. 4517104 A. The use of copolymers derived from ethylene and one or more C_3-C_{28} α-olefins and grafted with an ethylenically unsaturated dicarboxylic acid and subsequently reacted with a polyamine with at least two primary amine groups have been described in U. S. Patent No. 4137185 A. The most effective viscosity modification was found for the polymers with molecular weight ranging from 10,000 to 500,000.

Some multifunctional additive composition comprising of copolymer of ethylene and at least one C_3-C_{10} α-olefin and optionally a polyene selected from nonconjugated dienes and trienes have been reported in the U. S. Patent No. 4863623. The additive is also claimed to have antioxidant and dispersant property. The use of ethylene-α-olefin polymer for improving the viscosity index was reported in U. S. Patent No. 5151204 A. The α-olefin contained 1 to 18 carbon atoms in the alkyl chain with a number average molecular weight from 20,000 to 500,000 and with terminal ethylidene unsaturation in at least about 30 % of the polymer chains.

The U. S. Patent No. 5356551 disclosed the synthesis of multifunctional additive for lubricating oil exhibiting dispersant, low temperature and viscosity modification properties. The additive with number average molecule weight from about 5,000 to 500,000 consist of at least one C_3-C_{28} α-olefin monomer grafted with ethylenically unsaturated carboxylic acid having 1 or 2 acid or anhydride moieties such as succinic acid or anhydride. Additive based on vinyl aromatic/conjugated diene and ethylene/C_3-C_{18} α-olefin of specific structure and composition has been described in U. S. Patent No. 4194057 A. The additive composition also contains a polybutene of defined molecular weight and is reported as excellent viscosity index improver. A lubricating oil composition of an oil soluble copolymer of ethylene and C_3-C_{18} higher α-olefins have been disclosed in U. S. Patent No. 4088589 A with significant viscosity index improving properties. The additive is also reported to improve the low temperature performance when the copolymer contains a minor weight proportion of C_{10}-C_{18} alkyl acrylate or methacrylate.

The U. S. Patent No. 3897353 A described additive compositions of ethylene-propylene copolymers working as VIIs and alkyl methacrylates working as PPDs. The favourable carbon number of the alkyl portion of the ester is reported between 12 to 18 carbon atoms. Another class of poly methacrylate additive have been reported in U. S. Patent No. 4956111 A with molecular weight from 10,000 to 300,000 and with an average alkyl group chain length from 12.6 to 13.8 capable of reducing the pour point to -35^{0}C along with detergent and viscosity modification properties. The U. S. Patent No. 4668412 described the synthesis of additives containing terpolymer of stearyl methacrylate, maleic anhydride and lauryl methacrylate which has been formulated with dimethyl amino propyl amine and mannich base of amino ethyl pyparazine,

paraformaldehyde and 2, 6-ditertiarybutyl phenol. The additives are reported to act as dispersant VII and PPD.

The use of a lubricating oil composition containing mineral oils is reported in U. S. Patent No. 4886520 A which showed more enhanced VII and PPD properties by the addition of a terpolymer containing an olefinically unsaturated homo or heterocyclic nitrogen compound, alkyl ester of an unsaturated monocarboxylic acid and an allyl acrylate or methacrylate or a perflouro alkyl ethyl acrylate or methacrylate.

From the above literature study, it was found that a lot of work has already been done on acrylate, methacrylate and olefin polymers with varying structure and morphology for improving the pour point and viscosity index of lubricating oils. However, the reports regarding their multifunctional performance are very scanty. Also, the acrylate and methacrylate based polymeric additives are among the most widely used commercial additives for lubricating oils. Moreover, with the new standards regarding the emissions of gases and with the associated changes in the engine designs, it was felt necessary to further explore this area of chemistry and develop multifunctional additives with superior performance, reduced cost and better fuel economy. Keeping this in mind, the author has synthesized homopolymers and copolymers of acrylates and methacrylate of different alcohols and evaluated their performance as VII and PPD in different types of base oils. The different acrylates and methacrylate used are octyl acrylate, decyl acrylate, dodecyl acrylate, behenyl acrylate, undecyl methacrylate and myristyl methacrylate while the other monomer unit used for synthesizing copolymers is 1-octene. The results of the present investigation would undeniably facilitate the development of some superior and efficient multifunctional additives having both PPD and VII properties for lube oils.

References

References are given in BIBLIOGRAPHY under Chapter-I of Part-I (Page No. 188-194).