Part I

Methacrylate based polymeric additives as multifunctional lube oil additives

Chapter I

Background of the present investigation

In recent years, the Original Equipment Manufacturers (OEM) are developing modern and advance engines. The advanced engine technology requires the development of new lubricants and improvement of the existing one. As a result, the productive sector and the regulatory agencies must develop methods and mechanism to monitor cost effectiveness and the performance of the products available in the market. In order to cope up with this present demand it is essential to synthesize some multifunctional lube oil additives that not only increase the lifetime of lubricating oil but also increase the lifetime of engine at a cheaper cost. The use of multifunctional additive in lubricating oil formulation is well known.[1] All commercial lubricants contain some additives to add additional their performances in them. The percentage of additives in lubricants may vary from 1% to 30% or more.[2] The different types of lubricating oil additives are (a) pour point depressant (PPD)[3] which decreases the pour point of lube oil by dissolving the wax present in lube oil, (b) viscosity index improvers (VII)[4] which increases the viscosity index so that the lube oil does not change its viscosity appreciably with temperature change, (c) antioxidant which increases thermal stability[5], (d) anti wear which prevents direct metal to metal contact[6], (e) detergents /dispersants[7], (f) corrosion inhibitors[8], (g) extreme pressure additives[9] etc. These additives when added to lubricating oil enhance the properties already present or add some new properties also. Keeping in view the cost and the harmful nature of the chemicals used in this field, demand for multifunctional additive is increasing. In recent context, multifunctional additives play the major role in the technology of engine oils. Research throughout the world is directed to produce multifunctional lube oil additives.[10]

In accordance with the present investigation, it will be very pertinent to include a brief review on VII and PPD property of methacrylate based polymeric additives for lube oil.

As discussed in the general introduction, a viscosity index improver (VII) is explained in terms of viscosity index (VI) which is an arbitrary number[11] that indicates the resistance of a lubricant to change in viscosity with increase in temperature. Viscosity index improvers are compounds which increases the viscosity index of lubricant. A higher viscosity index indicates small change in viscosity with rise in temperature and vice - versa. Again productiveness of a VII depends on the type and concentration of the additive. Long chain high molecular weight polymeric additives are generally used as VII. Performance of the VII depends on the behaviour of the polymer molecules in the lube oil in terms of solubility and

resistance to shear degradation.[12] The solubility of polymer molecule increases with increasing temperature and the polymer molecules change from tight coils to an open configuration which has a greater volume. This increase in volume causes increase in viscosity of the oil, which offsets the normal reduction of viscosity with increasing temperature.[13, 14] The polymer having high molecular weight also increases the effective volume in an oil solution and as a result, a polymer having higher molecular weight also exhibits higher viscosity index than a lower molecular weight polymer of the same type.[15]

Pour point depressants are designed to prevent the agglomeration of wax particle present in lube oil. If lubricating oil is not properly protected with pour point depressants, the flow characteristic of lube oil is highly affected which can affect the engine performances. The polymeric additives which are used as pour point depressant must have some pendant alkyl groups and there should be a appropriate distance between the pendant chains and there must be a suitable ratio of monomers if copolymer is used as a PPD.[16, 17] Pour point depressants used earlier were either alkylated aromatic polymers or comb polymers.[18] Comb polymers have long alkyl chains attached to the backbone of the polymer, with the alkyl group being of different carbon chain lengths. Earlier the mechanism action of PPD was assumed that the alkylated aromatic compounds function by coating the surface of the wax crystals and preventing further growth. More recently, it is believed that PPD function by nucleation, co-crystallization or adsorption and disrupting the formation of three dimensional wax crystals network.[19]

The homo and copolymers of alkylmethacrylate or alkylacrylate are widely used as viscosity index improver (VII), commonly known as viscosity modifier (VM) and pour point depressant (PPD). The alkylmethacrylate polymers are more polar than ethylene/propylene or styrene/diene polymers and the long chain alkyl group imparts solubility to the lube oil. A mixture of methacrylates monomer having different alkyl chain can be copolymerized in a identical copolymerization reactivity ratio and in a statistically random distribution regardless of the size of the alkyl groups.[20] Most of the additives used as VM and PPD for lubricating oil are methacrylate and acrylate based polymers. The following patents discussed the same.

U.S. Patent No. 5834408 described the procedure of synthesis and performance evaluation of acrylate based copolymers as a PPD in lube oil compositions. U.S. Patent No. 4867894 claimed that copolymers of methyl methacrylate having an average molecular weight from 50,000 to 500,000 showed excellent pour point depressants for petroleum oil.

U.S. Patent No. 4073738 described the application of alkyl acrylate or alkyl methacrylate as pour point depressants for lube oil where in the alkyl group can have 8 to 22 carbon atoms. U.S. Patent No. 3897353 disclosed the oil composition comprising lubricating oil and an n-alkyl methacrylate as a pour point depressant. These acrylates may be made from monomers wherein the alkyl group may have 12 to 18 carbon atoms.

Patent No. EP 0140274 described the application of lubricating oil additives which contain n-paraffin based polyalkylmethacrylate and acrylate. U.S. Patent No. 4490267 disclosed the synthesis of alkylmethacrylates based lubricating oil additives having carbon number C_1-C_{30}.

U.S. Patent No. 4073738 claimed that acrylate and methacrylate based copolymers with conjugated dienes exhibited high shear stability and useful as a VII for lube oil. U.S. Patent No. 5955405 claimed that methacrylate copolymers comprising of 5 to 15 wt% butyl methacrylate, 70-90 wt% C_{10} to C_{15} alkyl methacrylate and 5-10 wt% C_{16} –C_{30} alkyl methacrylate exhibit excellent low temperature properties in lubricating oils. U.S. Patent No. 4968444 described the use of mixed polyacrylates as multifunctional lube oil additives.

U.S. Patent No. 8105990, 3607749 and 4203854 described the application of poly methacrylate as viscosity modifiers for lubricating oil.

A number of literatures are available on efficiency of poly alkyl acrylate and poly alkyl methacrylate as VII and PPD.[21-23] In 1937, Rohm and Haas Co. patented the first polymeric pour point depressant, poly alkyl methacrylates (PAMAs). Almost 15 years later Ruehrwein reported the action of n- alkyl poly methacrylate as PPD in the series dodecyl, tetradecyl, hexadecyl and octadecyl methacrylate.[24]

In 1997, El- Gamel et al. reported the synthesis of alkyl methacrylate – C_{18} α-olefin as PPD for waxy residue fuel and concluded that the polymer containing alkyl group consisting of 21 carbon number showed excellent pour point depressant.[25] In 2010, Rasha et al. had reported a novel PPD for waxy crude oil based on alkyl acrylates terpolymers.[26]

In 1949, W. L. Van Horne reported polymethacrylates as VII and PPD in a number of lubricating base stocks.[27] In 2010, Jukic et al. studied the thermal stability of n-alkyl methacrylates and styrene based terpolymers. The research group reported that the terpolymer consisting of dodecyl methacrylate (DDMA), octadecyl methacrylate (OCMA) and styrene as monomers has a good thermal stability.[28]

In 2010, A. M. Nassar reported six copolymers of 2- ethylhexyl methacrylate with vinyl acetate at different molar ratios. The performance of these polymers in lube oil was evaluated as VII and found that efficiency increases with increasing molecular weight of polymers as

well as concentrations in lube oil.[29] In 2011, Jung et al. reported twelve copolymers and six terpolymers based on different methacrylates and performance of these polymers in lube oil were evaluated as PPD. The research group reported that the terpolymers made from dodecyl methacrylate, hexadecyl methacrylate and methyl methacrylate at a molar ratio of 3.5:3.5:3 exhibited the best low temperature properties.[30]

In 2012, Jukic et al. reported the application of polymer made from dodecyl methacrylate (DDMA), octadecyl methacrylate (ODMA), N, N dimethylaminoethyl methacrylate (DMAEMA) with styrene as VII, PPD and detergents/dispersants. The research group reported that by increasing the percentage of DMAEMA in copolymer from 2 to 10 mol%, their M_w values decreases from 120 to 60 kg mol^{-1}.[31] In 2012, Mohammed et al. reported poly methylmethacrylate as additive for Iraqi lubricating oils in engine condition and performance evaluation was viscosity index improvement.[32]

In 2006, Abdel-Azim et al. reported twenty polymeric additives based on different ratios of styrene and different esters of acrylic acid. The efficiency of the polymers in lube oil was evaluated as PPD. The research group reported that the efficiency as PPD decreases by increasing the styrene content in the prepared polymers.[33] In 2007, Jukic et al. reported styrene, dodecylmethacrylate and octadecyl methacrylate based terpolymers as viscosity index improvers for lubricating oil. The research group also cited that the content of styrene in the terpolymer was limited up to 25% by weight and VI increases with increasing molar mass and opposite effect was obtained by increasing the styrene content.[34]

From the above literature study, it is seen that lot of works already done on polymethacrylate as additive for lubricating oil. Since methacrylate based polymeric additives are widely used as a commercial lube oil additives, therefore, further explorative studies on the methacrylate based additives were felt necessary to obtain still better performance out of this chemistry. Keeping this view in mind, the present investigation comprises the synthesis and characterization of homo and copolymers of decyl and dodecyl methacrylate and evaluation of their performance as VII and PPD in different types of base oils.

References

References are given in bibliography section under Chapter I of Part I (Page No. 178 - 180).