

PART-I

ACRYLATE POLYMERS AS MULTIFUNCTIONAL LUBRICATING OIL ADDITIVES

CHAPTER-I

BACKGROUND OF THE PRESENT INVESTIGATION

The lube oil is the building block with respect to which appropriate additives are selected and well blended to achieve a delicate balance in performance characteristics of the finished lubricant. The lube oils are products of refining crude oil. They are complex mixture of aromatic, paraffinic, and naphthenic hydrocarbons with varying molecular weights. The proportions of different hydrocarbon components determine the characteristics of the base oils.

Lube oil Additives are chemical compounds added to lube oils to provide specific properties to the finished oils. Some additives impart new and valuable properties to the lubricant; some develop properties already present, while some additives reduce the rate at which undesirable changes take place in the product during its service life. Recent research towards the understanding of additives performance in base oils indicated that the performance of additives when used in lubricating oil and applied in field conditions are very much dependent on the structure and morphology of the polymer dissolved in it.

Additives cover a varied range of chemicals, simple organic molecules, polymers, inorganic compounds etc. In base oil single or mixture of additives can be used as needed. In absence many of these, the oil would not accurately protect engine parts at all functioning temperatures, become contaminated, break down. Some additives impart lubricants to perform better under severe conditions, such as extreme pressures and temperatures and high levels of contamination. Combination of different additives and their quantities are determined by the lubricant type (Engine oils, Hydraulic oils, Gear oils, cutting fluids, compressor oils, Way lubricants, etc.) and the specific operating conditions (temperature, loads, machine parts materials, environment). Additives help lubricants withstand extreme operating environments. Even the best base oil cannot protect as well against the effects of heat, shearing forces, chemical and water dilution, corrosion and wear particles. In short, additives make good base oils better.

Considering the performances, the additives can be of different types as follows:

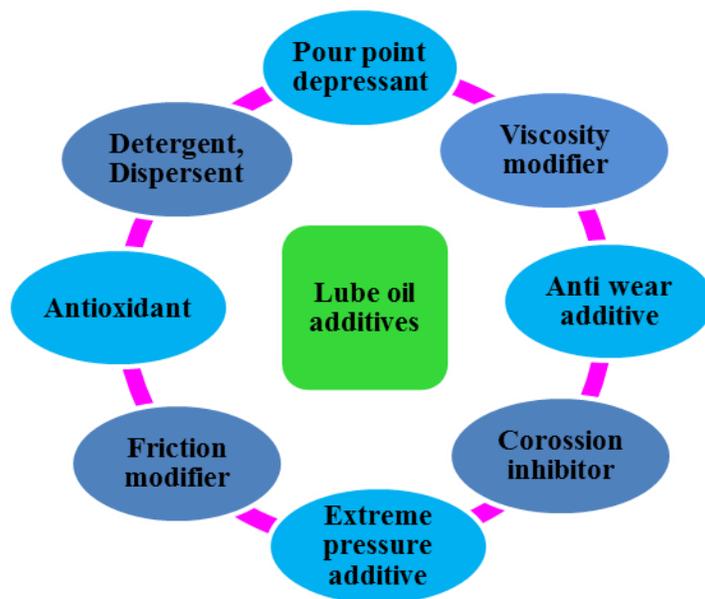


Figure 1(a). Different kinds of lube oil additives

These additives when added in base lubricating oils improve their field performance by providing their natural characteristics. The additives, single or mixture, provide special performance to meet the requirement of the base oil in field application. Considering the cost effectiveness, demand and research for multifunctional additive¹⁻⁵ i.e. a single additive wherein more than one additive performance can be present⁶⁻⁹ are increasing. Recently multifunctional additives play the major role in the technology of engine oils.

With this background the present investigation involves the incorporation of few major additive performances (PPD, VM, shear stability) in single additive system.

In keeping with the present investigation, it will be very relevant to include a brief review on PPD and VM additives of lubricating oil. Several investigations together with lot of experience of high molecular weight compounds as additives in use till now are opening

possibilities in the development of multifunctional polymeric additives that have both PPD and VM properties.

The lowest temperature at which lubricating oil will maintain its fluidity when cooled under specific conditions¹⁰⁻¹⁴ is called pour point. Most mineral oils have some dissolved wax and as the oil is cooled, some of the waxy materials of the lube oil come out of solution as tiny crystals. As the temperature decreases, progressively more wax precipitates. Gradually the wax crystals grow in size and finally, form a three-dimensional rigid structure for which the oil entirely loses its ability to flow under the test conditions. Although the wax network containing trapped oil is somewhat brittle and easily destroyed by shaking or stirring but in many applications like an oil reservoir where the bulk of the oil is in a stagnant situation, the wax structure inhibits oil flow ability very effectively. Thus there is a lower temperature bound on the lubricant application, consequently, addition of certain external material termed as Pour Point Depressant¹⁵⁻¹⁹ (PPD) is needed. Certain high molecular weight polymers with long chain hydrocarbon can reduce the pour point temperature of the lube oil and thus developing low temperature flow performance. PPD function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperature. The mechanism of action of PPD involves modification of large wax crystal network formation by preventing wax crystals from agglomeration or solidification at reduced temperatures. The efficiency of a PPD depends on their, structural properties, chemical composition and alkyl chain length. Their structural linearity assists to prevent the wax crystal growth by co-crystallizing with the wax species present in the oil. Furthermore, the wax crystals are remain apart from each other by the PPD backbone which adsorbed in wax crystal. Thus the wax in the oil remains as tiny particle and is no longer able to form three-dimensional structures to inhibit flow and ensure fluidity.^{20, 21} Most common PPD's

are fumarate copolymers,²² ethylene-vinyl acetate copolymers,^{23, 24} poly (methacrylates),^{16, 25} poly (acrylates)²⁶ etc.

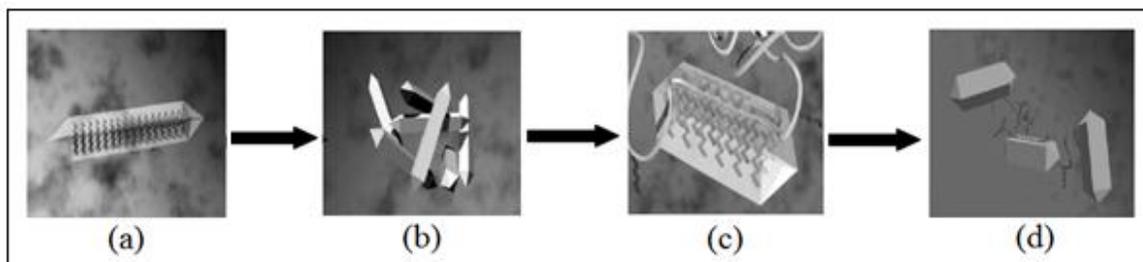


Figure 1(b): PPD action mechanism showing four stages, a) needle of oil, b) gel network formation at low temperature, c) co-crystallization of PPD with needle like structure, and d) deformation of crystal network.

In selecting the proper lubricant²⁷⁻²⁹ for a given application, viscosity is an important property to consideration. The viscosity of a liquid determines resistance to flow of a fluid. There is inverse relation between viscosity and fluidity. As the oil tends to thin out at high temperature viscosity inversely varies with temperature. The viscosity index³⁰⁻³¹ is an indicator of the change in viscosity as the temperature is changed. Higher VI³⁰⁻³¹ reveals lesser change of the viscosity of an oil for a given temperature change. Viscosity index improvers (VIIs) or Viscosity Modifiers (VMs)^{32, 33} are used to prevent the rate of change of viscosity with temperature and keep almost the same viscosity at all temperatures. Also efficiency of a VM depends on type, structure and concentration of the added polymer.

Polymers having long chain, high molecular weight are generally used as VM.³⁴ Performance of the VII depends on its behavior in the lube oil such as its solubility, resistance to shear degradation³⁵ etc.

In cold oil the polymer molecules remain as coiled form so that their influence on viscosity is minimized. In hot oil, the polymer molecules tend to straighten out, so the interaction between

these molecules and the oil provide a proportionally greater thickening effect.

The results of the investigation³⁶ of Michael J. Covitch et al. relating measurement of polymer coil sizes of VMs by both intrinsic viscosity and Small Angle Neutron Scattering (SANS) showed that it is not coil size growth with temperature is essential mechanism to explain elevation of viscosity index rather the polymers which grow with temperature have more VI contributions than those other.

Polymers having high molecular weight are used as lube oil additives in mainly three applications: viscosity index improvers, pour point depressants, and polymeric dispersants. Viscosity index improvers along with polymeric dispersants, make possible to design of high quality multigrade oils. Viscosity index improvers are oil-soluble polymers with molecular weights range from 8,000 to over 1,000,000.

The noticeable function of the viscosity index improver is to improve the temperature-viscosity relationship of the finished oil. The polymer molecule in solution exists as a polymer coil which is swollen by the hydrocarbon solvent. The degree of swelling or voluminosity of this coil determines the degree to which the polymer increases viscosity.

In addition to viscosity index, thickening power and pour point the shear stability is a vital property in determining the performance of a polymer. When a polymer added oil is subjected to high shear rates under conditions of turbulent flow, polymer backbone may be physically cleaved.

The shear stability of a polymer, its ability to resist such cleavage, is measured by subjecting the oil solution to cavitation in an ultrasonic generator. The result of polymer cleavage is a loss in viscosity. While it is economically attractive to use high molecular weight polymers because of their high thickening power and viscosity index their inferior shear stability results in

a rapid loss of viscosity in service. It is therefore necessary to get an optimal relation between viscosity index improving qualities and viscosity loss. It is often stated from the practical viewpoint of polymer design and lubricating oil formulation that the critical factor that controls shear stability is the average molecular weight of the particular class of polymers used.

So, Shear stability of the VM is one of the significant criteria that determine its suitability in a lubricant formulation. The shear stability of the additive provide a strong influence on multigrade engine oil's to perform as viscosity modifier under shearing conditions, experienced by the lubricant while in use. The loss of viscosity of a lubricant under shear can be of two kinds, namely temporary viscosity loss (TVL) and permanent viscosity loss (PVL). The PVL occurs due to mechanical degradation of polymer molecules, and can be determined using a standard shearing test such as Diesel Injector Shear stability Test (DISST) as per ASTM D-3945 method. The PVL values are more frequently expressed in terms of permanent shear stability index (PSSI). The equations are as follows:

$$PVL = (V_i - V_s)/V_i \times 100$$

$$PSSI = (V_i - V_s / V_i - V_0) \times 100$$

Where V refers to kinematic viscosity (KV), $V_0 = KV$ of the solvent before addition of polymer, $V_i =$ Initial KV of the solvent with polymer, $V_s = KV$ of the solvent after shearing.

Thus only a few investigations have been so far carried out on the properties of lubricant compositional parameters such as polymer concentration, polymer type, base oil viscosity etc. on the shear stability performance of multigrade lubricants.

Thus, as a part of continuing studies on mechanical and thermo-oxidative degradation of viscosity modifier, further studies were taken-up in this area considering possible generalisations on the effects of various parameters on shear stability performance of multigrade lubricants.

The observation of the previous researchers in accordance with the present line of investigation regarding PPD, VM and shear stability is being presented, in a selective manner, in the following paragraphs.

It was well accepted that the polymers having longer alkyl chains effectively depress the pour point of the oil with high temperature whereas the polymers having shorter alkyl chains are more effective on the low temperature oils.

Gavlinet al.³⁷ studied some acrylates and methacrylates for their PPD properties. They selected dodecyl poly (methacrylate) for early work because it was the first acrylate based polymer observed by the authors act as active pour point depressant. Borthakur et al.²² synthesized many alkyl fumarate-vinyl acetate copolymers and the efficiency of these copolymers as PPD was experimented on Indian crude oils.

Some esterified copolymers with different fractions of maleic anhydride and α -olefin (the average carbon number is 18), called as EsMAOC polymers were synthesized by Liao et al.^{18,38,39} and their PPD ability was tested in crude oil.

Abdel Azim et al.²⁶ compared the pour point depressing ability of twenty polymeric additives synthesized from different fractions of styrene with different acrylate ester. T. T. Khidr⁴⁰ synthesized four esterified α -olefin maleic anhydride copolymers made from 1-octene or 1-tetradecene and maleic anhydride and esterified with dodecyl or NAFOL 1822B alcohol. The PPD efficiency of the copolymers in crude oil was tested and found that the alkyl chains of the prepared copolymers are an essential factor for a profound interaction of the additives with the crude oil. In other work,⁴¹ five copolymers were prepared from cinnamoyloxy ethyl methacrylate and octadecyl acrylate with alteration of molar concentration of the monomers and their PPD efficacy and rheological properties for two different waxy crude oils were studied with different

concentrations of the prepared additives. In a related work⁴², some terpolymers were synthesized from, octadecyl, hexadecyl ordocosanyl acrylate and maleic anhydride using varied compositions of the alkyl acrylates and their PPD efficacy was tested.

T. T.Khidr⁴³ prepared some terpolymeric and copolymeric additives of acrylates having different alkyl chain length with maleic anhydride. The prepared polymers were studied and found that they can perform both as PPD and wax dispersants for paraffinic oils. In 1949, W. L. Van Horne observed that poly (methacrylates) can effectively act both as PPD and VM⁴⁴. In related work Ghosh et al.⁴⁵ prepared homopolymer of methyl methacrylate and its copolymer with styrene and then the PPD property of the homo and copolymers were tested, compared and discussed.

S. Port et al. studied the polymers and copolymers of vinyl esters having long chain fatty acids such as polyvinyl caprylate, polyvinyl palmitate and copolymers of vinyl acetate with vinyl palmitate and found that they are active viscosity index improvers for lubricating oils. Also the effect is enhanced by the increasing⁴⁶ of the solubility and concentration of the polymer in lube oil. In the experiment of Yorulmaz³¹ the effect of size of the alkyl group, degree of alkylation, and molecular weight of different alkylated polystyrenes on its VI improving power were studied. Bataille et al. studied on synthesis and characterization of VI improver for naphthenic and paraffinic base oils.⁴⁷ Fernanda M. B. et al. performed a relative study between ethylene-propylene copolymers and hydrogenated styrene-diene copolymers to test their application as VI improvers in multigrade engine oils.⁴⁸ Pourhossaini et al. prepared copolymers olefin copolymer which was found to be a good viscosity modifier at low concentration in motor oil formulation⁴⁹. Nassar et al.⁵⁰ studied the efficiency as viscosity modifier of some acrylate based polymeric additives synthesized by copolymerization of different acrylates (decyl, 1-dodecyl, 1-tetradecyl, and hexadecyl) with different moles of styrene. They observed the VM

property increases as the molecular weight of the prepared copolymers increases. N. S. Ahmed synthesized polymers of different dialkylmaleates with two different monomers (vinyl acetate and styrene). The efficiency of the prepared polymers as viscosity index improver was studied and observed that it increases with increasing chain length and molecular weight of the polymers and as well as with increasing the concentration of the polymers in base oil.⁵¹

Ahmed et al. synthesized some copolymers of different acrylates with vinyl acetate and maleic anhydride and studied the effect of molecular weight, alkyl chain length and concentration on viscosity index and pour point of the polymers.⁵² In a related work, four copolymers were prepared from styrene, vinyl acetate and n-butyl acrylate monomers. The VM property and PPD efficiency were tested using two Mexican crude oils.⁵³ Polymers of myristyl acrylate were prepared by two different methods viz. microwave assisted method and thermal method and their performances as PPD and VM were evaluated and compared.⁵⁴ Ghosh et al. studied on performance evaluation of homopolymer of methyl methacrylate and its copolymer with styrene and 1-decene as PPD and VM.⁵⁵ In another experiment, some terpolymers were prepared using tetradecyl and hexadecyl acrylate with styrene and vinyl pyrrolidone. The PPD and VM properties of the terpolymers were studied and compared.⁵⁶

In addition to PPD and VI properties shear stability of polymer also be studied.

Ghosh et al.⁵⁷ investigated the degradation stability towards mechanical shearing (shear stability) of poly (methyl methacrylate) (PMMA) and its copolymer with styrene at different level of concentrations.

Curt lindhe⁵⁸ investigated the impact of Viscosity index improver having high molecular weight on shear stability using poly methylmethacrylate polymer and observed that inferior shear stability of high molecular weight polymer results in a rapid loss of viscosity in service.

B. Jiang et al.⁵⁹ also studied on Shear Thickening in Dilute Polymer Solutions and its molecular weight dependency.

K. Mackenzie et al. indicated the Relationships between molecular geometry and the effects in his work.⁶⁰

The shear stability of three types of polymers, namely polymethacrylate (PMA), olefin copolymer (OCP) and hydrogenated styrene-isoprene copolymer (SIP) ,generally used as VMs in lubricants, has been investigated by Ghosh et al.⁶¹ Studies were briefly extended towards an understanding of the relationship between thickening ability of the polymers and their shear stability.

B. J. Hardy et al.⁶² also studied the correlation between viscosity building of polymer and its shear stability.

There has been a significant patent activity related with pour point depressants, viscosity modifiers and shear stability which comprise acrylate and olefinic compositions. Some of them are included in the review work.

U.S. Patent No. 5834408 discloses preparation and evaluation of acrylate based copolymers as aPPD in lube oil compositions. U. S. Patent No. 4906702 A discloses the ester polymer of unsaturated carboxylic acid of acrylic and methacrylic acid act as PPD for lube oil. U. S. Patent No. 3598737 A describes lubricant compositions containing oil soluble copolymers of alkyl esters of monocarboxylic acid selected from the group consisting of methacrylic acid, acrylic acid and mixtures thereof which are said to improve various characteristics including pour point.

U. S. Patent No. 2655479 A of Munday et al. is describes to a PPD consisting of equal proportions of a copolymer of decyl acrylate and an acrylic acid ester of a mixture of alcohols

derived from coconut oil and having an average side chain length of about 13.5 carbon atoms. U. S. Patent No. 3598736 A discloses the addition of small amounts of oil soluble copolymers of poly (methacrylates) (wherein the alkyl side chain contains 10 to 20 carbon atoms with an average between 13.8 and 14.8 carbon atoms) to lubricating oils to improve the pour point property.

U. S. Patent No. 4867894 A discloses that copolymers of alkyl methacrylates containing 16 to 30 carbon atoms, having linear alkyl group and an average molecular weight from 50,000 to 500,000 showed PPD properties of petroleum oil. Patent No. CA 2059825 C describes PPD for lubricating oils comprising an olefin copolymer which contains alkyl side chains having 8, 12 and 14 carbon atoms. Patent No. EP 0498549 A1 claims PPD for lubricating oils derived from α -olefin copolymers which contain alkyl side chains having 8, 12 and 14 carbon atoms. The three α -olefin monomers used are decene, tetradecene and hexadecene and the molecular weight of the copolymer is from 150,000 to 540,000. U. S. Patent No. 5188724 A contains similar disclosure comprising an olefin terpolymer prepared by the polymerization of three monomers selected from the group consisting of C10, C14, and C16 olefin hydrocarbons. These PPD additives contain alkyl side chains of average chain length 10.5 to 12.0.

U. S. Patent No. 3607749 discloses poly (alkyl methacrylates) preferably of molecular weight above 100,000 and more preferably above 350,000 as viscosity index improvers. U.S. Patent No. WO2012076676 A1 describes a viscosity index improver comprising a poly (alkyl methacrylate) polymer which contains 10 to 15 carbon atoms in the alkyl residue. U. S. Patent No. 5151204 A describes lubricating oil composition comprising ethylene- α -olefin polymer which exhibits improved viscosity index. The alkyl group of the α -olefin contains 1 to 18 carbon atoms and the polymer has a number average molecular weight from above 20,000 to about

500,000 and an average of at least about 30 % of the polymer chains contained terminal ethylidene unsaturation.

U. S. Patent No. 4194057 A describes viscosity index improver additive composition containing a vinyl aromatic/conjugated diene polymer of specific structure and composition as one component and an ethylene/C3-C18 α -olefin copolymer of specific composition and viscosity as a second component. Preferably, the composition also contains a polybutene of defined molecular weight.

U. S. Patent No. 4073738 A has claimed the use of alkyl acrylate or alkyl methacrylate as a pour point depressant in lube oil and a viscosity index improver comprising a special selectively hydrogenated copolymer of styrene and a conjugated diene. U. S. Patent No. 3897353 A discloses lubricating oil compositions comprising a viscosity index improver of ethylene-propylene copolymer and a pour point depressant of alkyl methacrylate. U. S. Patent No. 4956111 A describes the use of poly (methacrylate) polymer having an average alkyl group chain length from 12.6 to 13.8 with molecular weight 10,000 to 300,000 for the polymer which can reduce the pour point to -35°C and is compatible with other additives e.g. VM and detergents.

U. S. Patent No. 4088589 A discloses a lubricating oil composition containing a viscosity index improving amount of an oil soluble copolymer of ethylene and C3-C18 higher α -olefins.. U. S. Patent No. 6753381 B2 claims synthesis of olefinic polymer blends containing ethylene-propylene copolymer and their application as viscosity index improver with better low temperature property. The molecular weight of the polymer blends falls within 20,000 to 3,00,000. U. S. Patent No. 4032459 also discloses lubricating composition containing hydrogenated copolymers of butadiene and isoprene with PPD and VM properties, the average

molecular weight being between about 40,000 to 225,000. Patent No. 5356551 claims the synthesis of lubricating oil multifunctional viscosity index improver-dispersant additive exhibiting improved low temperature viscometric properties. The additive is an oil soluble ethylene copolymer with at least one C3-C28 α -olefin monomer, having a number average molecule weight from about 5,000 to 500,000 grafted with ethylenically unsaturated carboxylic acid material having 1 or 2 acid moieties or anhydride moiety such as succinic acid or anhydride.

U. S. Patent No. 4517104 A describes about oil soluble viscosity index improving ethylene copolymers, such as copolymers of ethylene and propylene and ethylene, propylene and diolefin etc. U. S. Patent No. 4668412 claims the synthesis of a dispersant VM and PPD of a terpolymer of maleic anhydride, lauryl methacrylate and stearyl methacrylate which has been formulated with dimethyl amino propyl amine and mannich base of amino ethyl pyrazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol.

Above literature clearly shows that people have used acrylate, methacrylate or olefin polymers as a PPD or VM and studied their shear stability. Reports are not adequate regarding their multifunctional performance and shear stability. Thus, it was felt necessary to develop shear stable multifunctional additives for the lube oils which will reduce the cost and may take care about the fuel economy. Keeping this view in mind, the present investigation carried on synthesizing homopolymers and copolymers of acrylates of different alcohols and evaluating their effectiveness as shear stable PPD and VM to achieve multifunctional performance. The homopolymers used are poly (decyl acrylate), poly (dodecyl acrylate), poly (myristyl acrylate) poly (isodecyl acrylate) and poly (isooctyl acrylate). The monomer unit used for synthesizing copolymers is 1-decene, styrene. Characterization of the prepared polymers was done by spectral (FT-IR, ¹H-NMR and ¹³C-NMR), thermogravimetric, gel permeation chromatography and

viscometric method. Considering the present need and the emphasis as given by the OEMs, the result of the present investigation would definitely develop some efficient shear stable multifunctional additives having both PPD and VM properties for lube oils.

References

References are given in Bibliography under Chapter-I of Part-I (Page No 175-182).