PART-I

ACRYLATE-α-OLEFIN COPOLYMERS AS LUBRICATING OIL ADDITIVES

CHAPTER-I

BACKGROUND OF PRESENT INVESTIGATION

The basic building unit of a lubricant is lubricating oil which is also known as base oil or lube oil. The lube oils are based on mineral oils which are products of refining crude oil. They are complex mixture of paraffinic, aromatic, and naphthenic hydrocarbons with varying molecular weights, desirable viscosities, densities, and distillation curves and acts as a carrier of additives.

The lube oil reduces friction between metal surfaces in mutual contact. It should perform a number of other functions including lubrication, cooling, cleaning, suspending, protecting metal surfaces against corrosive damage, low temperature flow ability, fuel economy, cost effectiveness etc. Modern equipment and internal combustion engines must be lubricated to prolong its lifetime. But in most of the cases classical base oils do not meet Original Equipment Manufacturer (OEM) needs or consumer requirements and frequent oil changes are required. Different additives[1] are added to the base oils in anticipation to improve their lubrication properties. The additives either enhance an already-existing property of the base oil or add a new desirable property. The examples of already-existing properties are viscosity, viscosity index, pour point, and oxidation resistance and the examples of new desirable properties include cleaning and suspending ability, antiwear performance, and corrosion control. The additives are selected depending on the necessary characteristics to formulate finished lubricants with the desirable performance levels. The success of achieving the highest levels of performance in finished lubricants depends in understanding the interactions of base oils and additives and matching those to the requirements of machinery and operating conditions to which they can be subjected.

Additives cover a wide range of chemicals, from simple organic molecules, polymers to inorganic compounds etc. They are used as single or mixture of additives in base oil. Without many of these, the oil would not properly protect engine parts at all operating temperatures, become contaminated, break down, and leak out. In presence of some additives, lubricants may perform better under severe conditions, such as extreme pressures and temperatures and high levels of contamination. Depending on the performances, the additives can be of different types as follows:

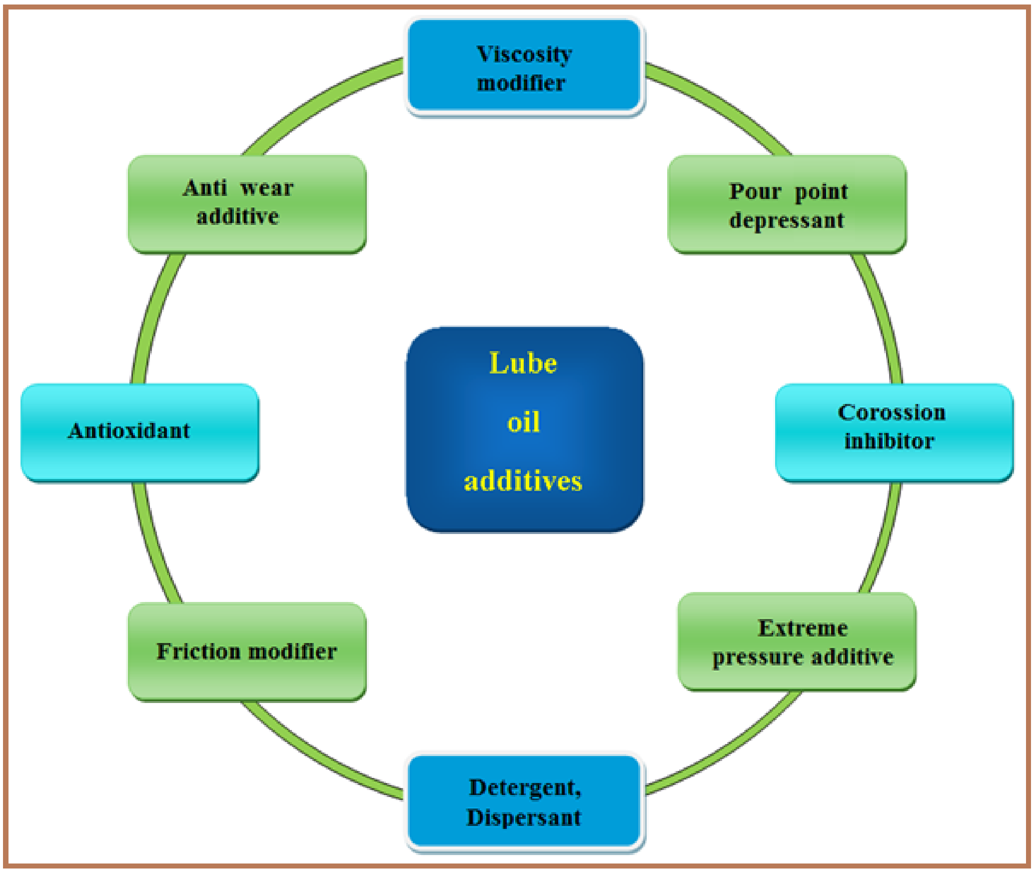

Figure 1(a). Different kinds of lube oil additives

These additives when incorporated in base lubricating oils improve their field performance in existing applications by supplying their natural characteristics. The additives as single or mixture can serve to meet the requirement of the base oil in field application. Keeping the cost effectiveness in mind, demand and research for multifunctional additive[2-5] i.e. a single additive in which more than one additive performance can be found[6-9] are increasing. Recently multifunctional additives play the major role in the technology of engine oils. With this background the present investigation comprises the incorporation of two major additive performances (PPD and VM) in single additive system.

In accordance with the present investigation, it will be very pertinent to include a brief review on PPD and VM additives of lubricating oil. Numerous investigations and the gathered 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 **Pour Point** (PP) of lubricating oil is the lowest temperature at which it will maintain its fluidity when cooled under specific conditions[10-14]. Generally most mineral oils contain some amounts of waxy materials and as the oil is cooled, some of the waxy components of the oil come out of solution as tiny crystals. With decreasing temperature, more and more wax precipitates. Thus the wax crystals grow in size and finally, form a three-dimensional network for which the oil completely loses its ability to flow under the test conditions. The wax network containing trapped oil is quite fragile and easily destroyed by shaking or stirring. However, in many applications like an oil sump or reservoir where the bulk of the oil is in a stagnant environment, the wax structure restricts oil flow ability very effectively. Thus there is a lower temperature limit on the lubricant application for which addition of certain external material known as **Pour Point Depressant**[15-19] (PPD) is needed. The flow characteristics of lubricants without PPDs can be adversely affected, causing a negative impact on engine performance. They are high molecular weight polymeric compounds with long hydrocarbon chain and can reduce the pour point temperature of the oil and thus improving low temperature flow performance. The effectiveness of a PPD depends on their chemical composition, structural properties, and alkyl chain length. The mechanism of action of PPD involves modification of large wax crystal network formation by preventing wax crystals from agglomerating or solidifying at reduced temperatures. Their structural linearity assists to modify the wax crystal growth by co-crystallizing with the wax species present in the oil. In addition, the wax crystals are kept apart from each other by the PPD backbone. Thus the wax in the oil retains 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 fumerate copolymers[22], ethylene-vinyl acetate copolymers[23,24], poly (methacrylates)[17,25], poly (acrylates)[26] etc.

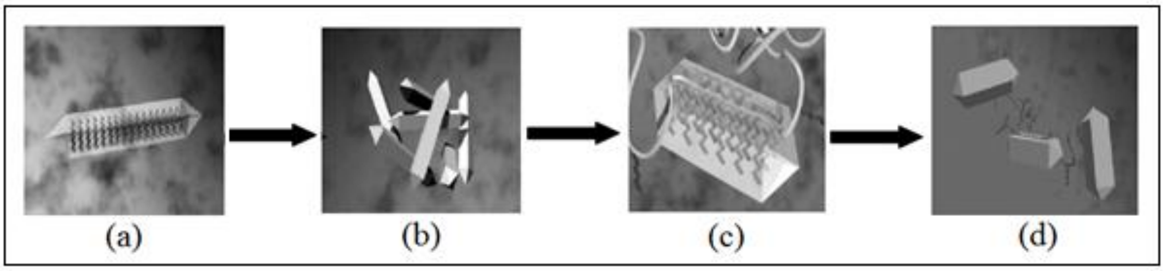

Figure 1(b): Mechanism of PPD action showing four stages, a) needle of oil, b) gel network formation at low temperature, c) co-crystallization of PPD with needle like structure, and d) deformation of crystal network.

Again, viscosity is a very important property of a lubricant[27-29]. The viscosity of a liquid is a measure of its resistance to flow. High viscosity oil is less fluid than the one of low viscosity. At higher temperatures, the oil tends to thin out, which results a reduction in viscosity and flows more readily and vice versa. **Viscosity Index** (VI)[30,31] is a parameter required to express the change in the viscous nature of the lube oil with temperature. The higher the VI, the less the viscosity of an oil changes for a given temperature change. **Viscosity Index Improvers** (VIIs) or **Viscosity Modifiers** (VMs)[4,32] are added to lubricating oils to make them behave as ideal lubricant which possess almost the same viscosity at all temperatures. Again effectiveness of a VM depends on the type and concentration of the polymer additive. Long chain high molecular weight polymer compounds are generally used as VM[5]. Performance of the VM depends on its behavior in the oil such as its solubility, molecular weight, and resistance to shear degradation[33]. The polymer changes its shape from tight coil to a straight chain configuration thus exerting a greater thickening effect on oil at higher temperatures than they do at lower temperatures. This thickening effect counterbalances the reduction of the viscosity of the lube oil at the elevated temperature[32].

The results of the experiment[34] of Michael J. Covitch et al. involving measurement of polymer coil dimensions of VMs by both intrinsic viscosity and Small Angle Neutron Scattering **(**SANS) indicated that coil size expansion with temperature is not required mechanism to explain significant elevation of viscosity index rather the polymers which expand with temperature have greater VI contributions than those that do not.

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

It was well documented that the polymers with longer alkyl chains are effective in depressing the pour point of the high temperature pour oils, while the shorter alkyl chain polymers are effective on the low temperature pour oils. Gavlin et al.[35] analysed some methacrylates and acrylates for their PPD properties. They chose dodecyl poly (methacrylate) for initial work because it was the first acrylic polymer observed by the authors to be an active pour point depressant. Borthakur et al.[22] prepared a number of alkyl fumarate-vinyl acetate copolymers and the efficacy of these copolymers as PPD was tested on indian crude oils.

Some esterified copolymers made of different ratios of maleic anhydride and α-olefin (the average carbon number is 18), called as EsMAOC polymers were prepared by Liao et al.[15] and their pour point depression ability was tested in crude oil and heavy diesel oil. Next year they prepared MOVAS copolymer[36] obtained from maleic anhydride, α-olefin and a mixture of vinyl acetate and styrene and evaluation of the additive as PPD was done. Later, they synthesized a viscous semi solid MOAS copolymer[37] from maleic anhydride, mixed α-olefins (the average carbon number is 15), acrylic alkyl ester and styrene. The prepared polymer was tested for pour point and Cold Filter Plugging Point (CFPP) of diesel fuel.

Abdel Azim et al.[26] compared the pour point decreasing effect of twenty polymeric additives prepared from different ratios of styrene with different esters of acrylic acid. T. T. Khidr[38] synthesized four esterified α-olefin maleic anhydide 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 another work[39], five copolymers were prepared from octadecyl acrylate and cinnamoyloxy ethyl methacrylate at different molar concentration of the monomers and their PPD efficiency and rheological characteristics for two different waxy crude oils were studied using different concentrations of the prepared additives. In a similar work[40], some terpolymers were prepared from docosanyl acrylate, octadecyl or hexadecyl acrylate and maleic anhydride using different compositions of the alkyl acrylates and their PPD efficiency was tested.

T. T.Khidr[41] again prepared some copolymeric and terpolymeric additives of acrylates of different alkyl chain length and maleic anhydride. The prepared polymers were tested and found that they can act both as PPD and wax dispersants for paraffin gas oils. Ghosh et al.[42] synthesized homopolymer of decyl acrylate and its copolymer with styrene and the PPD efficiency of the homo and copolymers were compared and discussed.

S. Port et al. analysed the polymers and copolymers of vinyl esters of the long chain fatty acids such as polyvinyl palmitate, polyvinyl caprylate and copolymers of vinyl palmitate with vinyl acetate and found that they are effective viscosity index improvers for lubricating oils. Also the effect is enhanced as the solubility of the polymer decreases and its concentration increases[43]. The effect of degree of alkylation, size of the alkyl group and molecular weight of different alkylated polystyrenes on its viscosity index improving power were analysed in the experiment of Yorulmaz[30]. Bataille et al. discussed synthesis and characterization of viscosity index improver for naphthenic and paraffinic base oils[44]. Fernanda M. B. et al. carried out a comparative study between ethylene-propylene copolymers and hydrogenated styrene-diene copolymers aiming at their application as viscosity index improvers in multigrade engine oils[45]. Reza et al. prepared copolymers made of α-olefins (ethylene and propylene) which were found to be a good viscosity modifier at low concentration in motor oil formulation[46]. Nassar et al.[47] studied the efficiency of some acrylate polymeric additives prepared by copolymerization of different acrylates (decyl, 1-dodecyl, 1-tetradecyl, and hexadecyl) with different moles of styrene, as viscosity modifier. The VM property was found to increase with increasing molecular weight of the prepared copolymers. N. S. Ahmed prepared polymers of different dialkyl maleates with two different monomers (vinyl acetate and styrene). The efficiency of the prepared polymers for improving the viscosity index of the base oil was studied and found to increases with increasing alkyl chain length and molecular weight of the prepared polymers and also with increasing the concentration of the polymers in base oil[48].

There are also some instances in which methacrylates and acrylates are found to act both as pour point depressants and viscosity modifiers. In 1949, W. L. Van Horne found that poly (methacrylates) can suitably act both as PPD and VM[49]. Ahmed et al. prepared some copolymers through polymerisation of different acrylates with maleic anhydride and vinyl acetate and studied the effect of alkyl chain length, molecular weight and concentration on pour point and viscosity index of the polymers[50]. In a similar work, four copolymers were synthesized from styrene, *n*-butyl acrylate and vinyl acetate monomers. The PPD efficiency and VM tendency were tested in two Mexican crude oils[51]. 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[52]. Ghosh et al. carried out performance evaluation of copolymer of decyl acrylate with styrene and also of their compatible binary (polymer-solvent) and ternary solutions (polymer-polymer-solvent), as PPD and VM[53]. In another experiment, different terpolymers were prepared using tetradecyl and hexadecyl acrylate with styrene and vinyl pyrrolidone. The PPD efficiency and VM properties of the terpolymers were evaluated and compared[54].

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

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. 3679644 A also contains the same disclosure. 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. U. S. Patent No. 5955405 discloses methacrylate copolymers comprising of 5-15 wt % butyl methacrylate, 70-90 wt % C_{10}-C_{15} alkyl methacrylate and 5-10 wt % C_{16}-C_{30} alkyl methacrylate as having excellent low temperature properties in lubricating oils. U. S. Patent No. 6458749 B2 discloses lubricating oil compositions of a mixture of selected high molecular weight and low molecular weight alkyl methacrylate made of 16-24 carbon containing alcohols. The composition is especially effective at satisfying different aspects of low temperature fluid properties for a broad range of base oils.

U. S. Patent No. 2655479 A of Munday et al. is directed 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. 5834408 A describes the preparation and evaluation of acrylate copolymers as PPD in lube oil compositions. U. S. Patent No. 4906702 A describes the polymer of ester of unsaturated carboxylic acid selected from the group consisting of acrylic and methacrylic acid as PPD for lube oil. U. S. Patent No. 3772196 A claims lubricating oil composition comprising a minor but effective pour point depressing amount of a PPD of the group consisting of copolymers of alkyl acrylates, copolymers of alkyl methacrylates and copolymers of nitrogen containing esters of the acrylic acid series. U. S. Patent No. 3598737 A discloses 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.

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. The copolymer is prepared by polymerization of three α-olefin monomers which are decene, tetradecene and hexadecane having molecular weight from 150,000 to 450,000. 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. Similarly, Patent No. EP 0498549 B1 claims the preparation of a pour point depressant terpolymer wherein the average alkyl side chain length is 10.5 to 12.0, made from the above mentioned olefin monomers. 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 C_{10}, C_{14}, and C_{16} olefin hydrocarbons. These PPD additives contain alkyl side chains of average chain length 10.5 to 12.0. U. S. Patent No. 4514314 describes an oil soluble alkyl ester copolymer which is useful as a PPD for lubricating oils. These copolymers have a number average molecular weight from 1,000 to 40,000, preferably 2,000 to 15,000 and optimally 2,000 to 8,000. These copolymers are of the class consisting of a C_{22}-C_{40} branched alkyl ester of a copolymer of C_2-C_{20} α-olefin and maleic anhydride and di(2[C_{22} to C_{40}] alkyl) fumarate-vinyl C_1-C_4 alkylate e.g. acetate copolymer.

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. 4203854 A discloses a stable lubricant composition consisting about 0.60 to about 1.75 percent of an oil soluble poly (methacrylate) viscosity index improver having a molecular weight in the range of about 100,000 to about 750,000. 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. 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. 4137185 A describes oil-soluble, derivatized ethylene copolymers derived from ethylene and one or more C_3-C_{28} α-olefins, e.g. propylene, which were grafted with an ethylenically unsaturated dicarboxylic acid material and thereafter reacted with a polyamine having at least two primary amine groups. The polymers with molecular weight ranging from 10,000 to 500,000 were found most efficient as multifunctional viscosity index improvers. 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. 4863623 claims an additive composition comprising copolymer prepared from ethylene and at least one C_3-C_{10} α-olefin and optionally a polyene selected from nonconjugated dienes and trienes. The copolymer acts as multifunctional viscosity index improvers with dispersant and antioxidant property. U. S. 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 C_3-C_{28} 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. 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/C_3-C_{18} 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. The alkyl portion of the ester contains 4 to 22, preferably 12 to 18 carbon atoms and includes mixtures. 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^{0}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 C_3-C_{18} higher α-olefins. The low temperature performance was markedly improved when the copolymer contains a minor weight proportion of ethylene pour point depressants comprising of an oil soluble polymer of C_{10}-C_{18} alkyl acrylate or methacrylate. 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 pyparazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol. 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. U. S. Patent No. 4886520 A discloses an oil composition containing mineral oils which showed more enhanced PPD and VM properties by the addition of a terpolymer comprising an alkyl ester of an unsaturated monocarboxylic acid, olefinically unsaturated homo or heterocyclic nitrogen compound and then an allyl acrylate or methacrylate or a perflouro alkyl ethyl acrylate or methacrylate. 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.

From the above literature survey on PPD and VM, it was found that people have used acrylate, methacrylate or olefin polymers for their application either as PPD or VM. Reports are scanty regarding their multifunctional performance. Thus, it was felt necessary to develop multifunctional additives for the lube oils which will reduce the cost and may take care about the fuel economy. With this view in mind, the present investigation had been undertaken in synthesizing homopolymers and copolymers of acrylates of different alcohols and evaluating their efficiency as PPD and VM to achieve multifunctional performance. The homopolymers used are poly (decyl acrylate), poly (dodecyl acrylate), poly (isooctyl acrylate) and poly (isodecyl acrylate). The monomer unit used for synthesizing copolymers is 1-decene, an α-olefin. Characterization of the prepared polymers was carried out by spectral (FT-IR, ^{1}H-NMR and ^{13}C-NMR), thermogravimetric 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 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. 182-188).