PART I

SYNTHESIS, CHARACTERIZATION AND VISCOSITY STUDIES OF HOMO AND COPOLYMER OF METHYL ACRYLATE AND EVALUATION OF THEIR VISCOSITY INDEX IMPROVER AND POUR POINT DEPRESSANT PROPERTIES IN LUBRICATING OILS

CHAPTER I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

Lubricants are the materials which improve the smoothness of movement of one surface over another. Lubricants are usually liquids or semi-liquids. . Lubricating oils (lube oil) are used to include all those classes of lubricating materials that are applied as fluids. The basic building block of lubricating oil is commonly known as base oil or base stock. The base oils are complex mixture of paraffinic, aromatic and naphthenic hydrocarbons with molecular weights ranging from medium to high values, which produce oils with desirable viscosities, densities and distillation curves Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. These additives are compounds or mixtures when incorporated in base lubricating fluids, supplementing their natural characteristics and improving their field service performance in existing applications. In lubricating oils most commonly used functional additives are Viscosity index improvers (VII), Pour point depressants (PPD), Friction modifiers (FM), Anti-wear agents and extreme-pressure additives, Antioxidant additives, Anti-foam agents, Rust and corrosion inhibitors, Detergent and dispersant additives etc.

Today, multifunctional additives play a major role in the technology of engine oils. Thus, research throughout the world is increasingly directed toward producing additives with more than one purpose (i.e., multifunctional additives) [1-7].

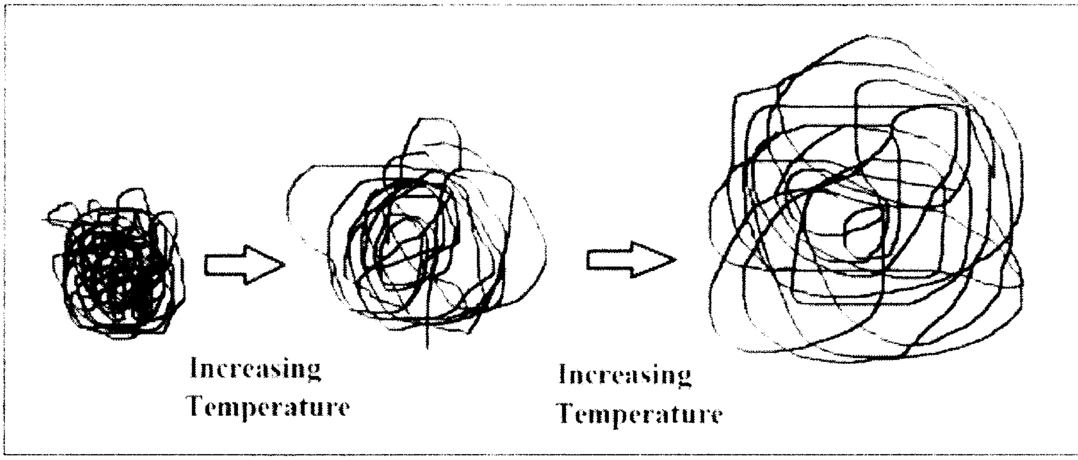
In accordance with the present invention, it will be very pertinent to include a brief introduction of multifunctional additives having both VII and PPD properties used in lube oil formulation, in this chapter.

Numerous investigation and the accumulated experience in use of high molecular weight compounds as additive to produce oil with given properties are now opening of possibilities in the development of multifunctional polymeric additives that have both PPD and VII properties.

Viscosity index (VI) term to express the VII properties is an arbitrary number [8], which indicates the resistance of a lubricant to viscosity change with temperature.

Viscosity index improvers are added to lubricating oils to modify the rate of change of viscosity with temperature. These improvers have little effect on oil viscosity at low temperatures. However, when heated the improvers enable the oil viscosity to increase within the limited range permitted by the type and concentration of the additive. This quality is most apparent in the application of multigrade motor oils.

Performance of viscosity index improvers depends on the behaviour of the polymer molecules in the oil. Polymer solubility, molecular weight, and resistance to shear degradation are the most important parameters [9]. The polymer molecule in solution exists as random coil [10], which is swollen by the lube oil solvent (**Scheme I**). Polymer solubility generally increases with increasing temperature as the polymer molecules change from tight coils to an open configuration, which has a greater volume. This increase in volume causes increase of the viscosity of the oil, which offsets the normal reduction in viscosity with increasing temperature [11-12].



Scheme I

Increasing polymer molecular weight also increases the polymer volume in an oil solution [13]. Consequently, a higher molecular weight polymer will import a higher viscosity index than a lower molecular weight polymer of the same type [14].

The pour point of lubricating oil is the lowest temperature at which it will pour or flow when it is chilled without disturbance under prescribed conditions [15]. Most mineral oils contain some dissolved wax, and as an oil is chilled, this wax begins to separate as crystal that interlock to form a rigid structure that traps the oil in small pockets in the structure [16]. When this wax crystal structure becomes sufficiently complete, the oil will no longer flow under the conditions of the test. Low pour points may be achieved by intensively dewaxing the oil during refining. However, the deep dewaxing of oil fractions decreases its oxidation stability and increases the tendency toward formation of carbon deposits. Certain high molecular weight polymers function by inhibiting the formation of a wax crystal structure that would prevent oil flow at low temperatures [17-20]. The chemical additives are synonymously referred to as pour point depressants, flow improvers, paraffin inhibitors, or wax modifiers. Pour point depressants have no effect on the crystallization temperature or the number of crystals formed. Their most widely accepted mechanisms of action include adsorption, co-crystallization, nucleation, and improved wax solubility [20-22]. The effectiveness of a pour point depressant depends on the chemical composition and structural characteristics of the polymer and the structural characteristics of the polymer and the length of the alkyl side chains [13, 23-24]. Although the removal of the last traces of wax from oils is difficult and expensive, pour point depressants provide an economical means of facilitating the proper flow of the oil in an engine at low temperatures [25-27].

Many different types of pour point depressants have been used in the prior art [28]. Previously used pour point depressants are predominantly oligomers having molecular weights of 1,000 to 10,000, or polymers which have molecular weights greater than 10,000. The earlier pour point depressants were either alkylated aromatic polymers or comb polymers. Comb polymers characteristically have long alkyl chains attached to the backbone of the polymer, with the alkyl groups being of different carbon chain lengths.

The observation of the previous researchers in concord with the present line of investigation is being presented, in a selective manner, in the following paragraphs.

Although Polymethylacrylates (PMA) are preferred type of VII in certain applications, they often contribute to enhanced formation of deposits in the engine due to thermal instability of these additives under high temperature conditions. The usual approach to overcome this shortcoming is to incorporate a dispersancy property into the VII. Dispersant versions of PMA type VIIs are usually derived from a nitrogen-containing methacrylate monomer or by grafting the PMA polymer with a nitrogen compound. Although dispersant-PMAs function as better VIIs as compared to parent PMAs, there is a risk of affecting certain beneficial properties associated with normal PMAs such as pour point depressancy and good shear stability; particularly in the case of grafted PMAs.

Thus, within the category of PMA type VIIs, considerable need and potential exists to develop polymers with improved performance.

In a recent communication A. A. A. Abdel Azim [29] has reported that, polymeric additive based on octadecene - methacrylate copolymer has been prepared and evaluated as multifunctional additive (VI, PPD, Dispersancy - detergent). The octadecene– MA copolymer reacted with different long chain alcohols to produce different types of ester which were than aminated with different types of amines. It was found that the efficiency of the prepared compounds as viscosity index increases with increase in the concentration of additive and increase in the alkyl chain length of that compound where as their efficiency as PPD increases with decreasing the concentration of prepared polymer.

In a similar work [30] has described a method to prepare a series of copolymer and terpolymers, derivative of alkyl acrylate and maleic anhydride. They investigated the influence of the structure of the copolymer and terpolymers, PPD properties were found to increase with increase in concentration in solution and they also gave better result when the alkyl chain length of the copolymer is similar to the composition of the n-paraffin in waxy oil.

Floeria et al [31] investigated the influence of chemical composition on the PPD properties of methacrylate copolymers as additive for lube oils, methecrylate-styrene copolymer and observed that the efficiency is related to the length of the alkyl side chain of the polymethacrylates and to the nature of the base oils.

U.S. Patent No. 5834408 described preparation and evaluation of acrylate copolymers as a PPD in lube oil compositions.

U.S. Patent No. 4867894 describes that copolymers of the methyl methacrylate having an average molecular weight from 50,000 to 500,000 showed pour point properties of petroleum oil.

U.S. Patent No. 4956111 describes the use of poly methacrylate polymer having an average chain length of alkyl group in the polymer ranging between 12.6 - 13.8 can reduce the pour point to 35^0 C and is compatible with other additive e.g. VII and detergents.

U.S. Patent No. 4906702 discloses the olefin copolymer of unsaturated carboxylic acid ester as PPD for lube oil.

U.S. Patent No. 4088589 discloses a lubricating oil composition comprising a lubricating oil and VII amount of an oil soluble polymer composition consisting of a specific amount of copolymer of ethylene α- Olefin showed multifunctional properties eg., PPD, VII properties.

U.S. Patent No. 4073738 discloses acrylate and methacrylate based copolymers with conjugated dienes exhibit high stability to shear and may be useful in particular as a VII.

U.S. Patent No. 4668412 has claimed the synthesis of a dispersant VII and pour point depressant of a terpolymer of maleic anhydride and lauryl methacrylate and stearyl methacrylate which has been formulated with dimethyl amino propyl amine and manich base of amino ethyl pyparazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol

U.S. Patent No 4032459 discloses lubricating composition containing hydrogenated butadiene-isoprene copolymers with PPD, VII properties.

U.S. Patent No. 5955405 discloses a methacrylate copolymers comprising from 5 to 15 wt% butyl methacrylate, 70-90 wt% C-10 to C-15 alkyl methacrylate, from 5-10 wt% C16 -C30 alkyl methacrylate as having excellent low temperature properties in lubricating oils.

U.S. Patent No 4886520 discloses an oil composition comprising mineral oils showed more enhance PPD and VII properties by the addition of a terpolymer comprising an alkyl ester of an unsaturated monocarboxylic acid, and olefinically unsaturated homo and heterocyclic nitrogen compound and then an allyl acrylate or methacrylate or a perflouro alkyl ethyl acrylate or methacrylate.

U.S. Patent No 6458749 discloses polymerization of a mixed methacrylate made of C16 – C24 carbon containing alcohols when polymerized are especially effective by satisfying different aspects of low temperature fluidity properties for a broad range of base oils.

E. Patent No. 0236844 B1 teaches pour point improving agents derived from methyl methacrylate. This patent fails to teach the specific copolymers as viscosity index improvers for lubricating oils.

Thus from the above literature survey it is observed that in most of the cases the recent development in the additive chemistry has either an additive with an improved VII properties or with a better PPD performances. But reports regarding the development of a multifunctional additives comprising VII – PPD properties are still limited.

Thus considering the present need and the emphasis as given by the original equipment manufacturers (OEMs), it is felt to undertake the present investigation towards the development of an efficient multifunctional additive having VM as well as PPD properties for lube oils.

The present invention is directed to novel use of poly methyl acrylate and its copolymer with styrene as viscosity index improvers and pour point depressants for lubricating oils.