

PART II

STUDIES ON SYNTHESIS, CHARACTERIZATION, POUR POINT DEPRESSANT AND VISCOSITY INDEX OF HOMO AND COPOLYMER OF ACRYLATES WITH STYRENE

CHAPTER I

1.1 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

Base fluids mineral oil generally cannot satisfy the requirements of high performance lubricants without using the benefit of modern additive technology. Additives are synthetic chemical substances that can improve lots of different parameters of lubricants. They can boost existing properties; suppress undesirable properties in the base fluids. They can assist each other (synergism) or they can lead to antagonistic effects. Some additives are multifunctional products that decrease the possibility of additives interfering with each other negatively. Additives are used to (a) reduce the oxidative or thermal degradation of an oil, (b) to lessen the deposition of harmful deposits on lubricated parts, (c) to minimize rust and corrosion, (d) to control frictional properties, and (e) to reduce wear. They are also employed to alter purely physical properties of oil such as viscosity / viscosity temperature relationship known as viscosity modifier (VM) or viscosity index improver (VII) and also to improve the low temperature flow properties of the lube oil that is pour point depressant (PPD).

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) (Akhmedov, 1987; Eckert and Wortel, 1972; Ford and Wood, 1971; Kapur et al., 1995; Mohamed et al., 1994; Ranney, 1978; and Schwab and Heilweil, 1976) [1-7].

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 not only PPD properties but also VM properties.

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

As a brief introduction of PPD has already been presented in chapter I of Part I, a short discussion only on VMs is presented here.

An ideal lubricant for most purposes would possess the same viscosity at all temperatures [8]. Although a few non-polymeric substances such as metallic soaps exhibit VI

improving properties [9] all commercially important VI improvers today are oil-soluble organic polymers. Suitable polymers exert a greater thickening effect on oil at higher temperatures than they do at lower temperatures [10]. The viscosity index is an indicator of the change in viscosity as the temperature is changed. Higher the VI, lesser the change in viscosity of an oil for a given temperature. Viscosity index improvers are used to limit 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. Viscosity index improvers are long chain, high molecular weight polymers that function by increasing the relative viscosity of oil more at high temperatures than they do at low temperatures. Generally this results from the polymer changing its physical configuration with increasing temperature of the mixture. It is postulated then in cold oil the molecules of the polymer adopt a coiled form so that their effect on viscosity is minimized. In hot oil, the molecules tend to straighten out, and the interaction between these long molecules and the oil produces a proportionally greater thickening effect. Although the oil polymer mixture still decreases in viscosity as the temperature increases, it does not decrease as much as the oil would alone [11].

Some of the polymers generally used commercially as VII, and known to possess certain inherent advantages and disadvantages in performance, are- i) Poly isobutylenes (PIBs), ii) Hydro-generated Styrene – isoprene copolymers, iii) Olefin copolymers (OCP); e.g. Ethylene- propylene copolymer, IV) Esters of styrene- maleic anhydride copolymers and v) Poly(alkyl methacrylates) (PMA).

Olefin copolymers (or OCP) used as viscosity index improvers conventionally comprise copolymers of ethylene, propylene and optionally, a diene. Small polymeric side chains do not exert a substantial viscosity modifying effect in oil. Polymerized propylene has one methyl branch for every two backbone carbon atoms. Ethylene polymer is substantially straight chained. Therefore, at a constant amount of polymer in oil (treat rate), an OCP having a higher ethylene content will display an increased high temperature thickening effect (thickening efficiency, or TE). However, polymer chains having long ethylene sequences have a more crystalline polymer structure. Crystalline polymers are less oil soluble than

amorphous polymers and as a result, the OCP can drop out of the oil, causing the plugging of engine filters (and the loss of the viscosity modifying effect). Further, OCPs having substantial crystalline segments have been found, again primarily at low temperatures, to interact with waxes in the oil, and other OCP chains, which results in uncontrollable increases in low temperature viscosity and, in extreme cases, the gelling of the lubricating oil. These problems have been found to manifest in Ziegler Natta polymerized OCPs containing greater than about 60 wt. % ethylene (herein after referred to as "high ethylene content OCPs").

Due to their molecular architecture, star polymers are known to provide improved shear stability compared to OCPs. VI improvers that are star polymers made by hydrogenation of anionically polymerized isoprene are commercially available. Anionic polymerization results in a relatively low molecular weight distribution (M_w/M_n). Hydrogenation results in alternating ethylene/propylene units having a composition comparable to a polymer derived from 40 wt. % ethylene and 60 wt. % propylene. These VI improvers provide excellent shear stability, good solubility and excellent cold temperature properties. However, improvements in the balance between the thickening efficiency and shear stability of star polymers remain possible.

U.S. Pat. No. 4,116,917 exemplifies certain star polymers comprising hydrogenated poly(butadiene/isoprene) tapered arms containing about 44.3 wt. % polymer derived from butadiene. Since butadiene initially reacts faster than isoprene when anionic polymerization is initiated with secondary butyllithium (the process described in the patent), a polybutadiene block is first formed. As the butadiene concentration is lowered through polymerization, isoprene begins to add to the living polymer so that, when the polymerization reaction is complete, the chain is made up of a polybutadiene block, a tapered segment containing both butadiene and isoprene addition product, and a polyisoprene block resulting in a living tapered polymer chains that, when coupled with divinylbenzene, produce a star polymer having a polybutadiene block positioned distal from the divinylbenzene-coupled core. The long ethylene sequences of these external hydrogenated polybutadiene blocks were found to cause the same low temperature performance problems associated with high ethylene content OCPs.

To provide an improvement in thickening efficiency, while maintaining low temperature performance, U.S. Pat. No. 5,460,739 suggests star polymers comprising triblock copolymer arms of hydrogenated polyisoprene/polybutadiene/polyisoprene. The hydrogenated polybutadiene block provides an increased ethylene content, which improves thickening efficiency. The patent suggests that, by placing the hydrogenated polybutadiene block more proximal to the nucleus, the adverse effect on low temperature properties could be minimized. Such polymers were found to provide improved low temperature properties relative to the tapered arm polymers of U.S. Pat. No. 4,116,917. However, when such polymers were provided with a hydrogenated polybutadiene block of a size sufficient to provide a credit in thickening efficiency, a debit in low temperature performance remained relative to the pure polyisoprene polymers.

Therefore, Among the OCPs, there remains a need for improved VI improvers that are capable of providing a good viscosity temperature relationship, without the associated reduction in solubility and cold temperature performance.

Although PMAs 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 VMs, considerable need and potential exists to develop polymers with improved performance.

In a recent communication AAA Abdel Azim [12] 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 [13] 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 [14] investigated the influence of chemical composition on the PPD properties of methacrylate copolymers as additive for lube oils, methacrylate- 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 5834408 described preparation and evaluation of acrylate copolymers as a PPD in lube oil compositions.

U.S. Patent 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 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 35⁰ C and is compatible with other additive e.g. VII and detergents.

U.S. Patent 4906702 discloses the olefin copolymer of unsaturated carboxylic acid ester as PPD for lube oil.

U.S. Patent 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 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 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 pyrazine, paraformaldehyde and 2, 6-ditertiarybutyl phenol.

U.S. Patent 4032459 discloses lubricating composition containing hydrogenated butadiene-isoprene copolymers with PPD, VII properties.

U.S. Patent 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 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 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.

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 VM properties or with a better PPD performances. But reports regarding the development of a multifunctional additives comprising VM – 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 of varied compositions (different sources).