

## **Part II**

### **Investigation on anti wear properties of some well known viscosity modifiers**

## **Chapter I**

### **Brief introduction of present investigation**

Base fluids mineral oils usually can't satisfy the requirement of high performance lubricants without using the benefit of additive. Additives are chemicals which either improve different properties of base oil or introduce not-existing function in the lube oil.<sup>1</sup> They can even suppress undesirable properties of base oil. Mainly additives are used to (i) reduce the oxidative or thermal degradation of base oil, (ii) to reduce wear and improve frictional property, (iii) to improve low temperature performance, (iv) to reduce deposit on parts of engine, (v) to maintain proper viscosity in wide temperature range.<sup>2-6</sup> When two or more additives are used in single base oil, they can synergise each other's performance or can result antagonistic effect. Sometimes a single additive can have two or more properties, they are called multifunctional additives. This kind is preferred over using blend of different additives for introduction of different performance.

Additives are desired to be effective in lowest reasonable quantity for reduced cost and chemical hazards. Another important factor is that they should not produce by products in engine operating condition. They should ideally perform in different viscosity range as viscosity of base oil always keeps changing with temperature. Being soluble in base oil is also a most important attribute of an additive.

All the factors discussed above lead the researchers towards formulation of multifunctional cost effective performance additive.<sup>7,8</sup> An enormous research has been devoted to the synthesis of technology friendly additives for modern engines. With the continuous improvement of modern engines demands for more efficient additives are also upraising. A challenge for additive chemist is to find suitable additive which will take care of variation of oil viscosity along with good thickening and shear stability. Technology has successfully concerned itself with the development of lubricating oil additive with effect to protect wear together with other performance e.g. viscosity modifier, detergent etc.

Of all kind of lube oil additives used, Viscosity modifier (VM) is one of most important. Viscosity modifiers are substances which decrease the rate of variation of viscosity with temperature. As mentioned earlier a viscosity modifier is described in terms of viscosity index (VI) which is an arbitrary number<sup>9</sup> that indicates the resistance of a lubricant to viscosity change with temperature. Addition of VM increases the VI of base oil in particular temperature range. Higher the VI greater is the resistance of oil viscosity with temperature. Viscosity modifiers should be thermally stable and be capable to work in wide temperature range.

An elaborate description of VM is already given in Chapter I of Part I.

Some of the popular VMs used commercially are poly isobutylene (PIB), hydrogenated styrene-isoprene copolymer (SIP), olefin copolymer (OCP), poly alkyl methacrylate (PMA), copolymers of polyacrylate etc. They are known to possess specific advantages as well as disadvantages.<sup>10,11</sup>

PMA are well known VM in lubricant industry, several researches has been carried out to maintain desired balance of high temperature and low temperature viscosity as well as better shear stability. Polyolefins are also found effective for the same purpose as PMA and they are more economical. Both of them have some advantages and disadvantages. PMA are very efficient to improve viscosity-temperature relation of base oil, and show some anti wear activity when used in high concentration. On the contrary their treating cost is high in industrial scale. Polyolefins result the same thickening property as PMA even in smaller concentration, but their VM property is weak. So to achieve viscosity modifier activity with good oil thickening these two kinds (PMA and polyolefins) can be combined in single system. Detailed literature studies on PMA type viscosity modifier is already given in Chapter I of Part I.

Olefin copolymers (OCP) conventionally comprise copolymers of ethylene, propylene and sometimes a diene. Smaller polymeric side chains do not exert substantial viscosity modifying effect in oil. Polymerised propylene has one methyl branch for every two backbone carbon atoms. On the other hand ethylene polymers are straight chained. Therefore, at a constant treat rate, an OCP having higher ethylene content will result in increased high temperature thickening effect.<sup>12,13</sup> However, polymers with long ethylene sequences results in more crystalline polymer structure. Crystalline polymers are less oil soluble than amorphous polymers and as a consequence, OCP polymers can drop out of the oil causing the plugging of engine filters and thereby showing less viscosity modifier effect. Again crystalline nature of OCP increase the chance of interaction of the polymer with the oil waxes in low temperature, which results in huge increase of low temperature oil viscosity and in extreme cases gelling of the lube oil. This is highly undesirable in low temperature engine operating condition.

Due to their molecular architecture star polymers are known to provide improved shear stability compare to OCPs.<sup>14,15</sup> Viscosity modifiers of this kind made by hydrogenation of anionically polymerised isoprene are commercially available. Anionic polymerization results in relatively low molecular weight distribution (Mw/Mn). Star-shaped polymers generally have lower internal viscosities than their linear analogues due to their smaller hydrodynamic radii and radii of gyration. This makes them favourable for use in fluids that require low viscosity such as lubricating oils in car engines. They provide better thickening effect along with high shear stability.

U.S. Patent No. 8415284 B2 described a lubricating oil composition and methods of operating an internal combustion engine to provide improved engine operation. The lubricating composition included a major amount of oil of lubricating viscosity and a minor amount of at least one olefin copolymer having a number average molecular weight greater

than about 10,000 up to about 300,000. The olefin copolymer is grafted with (A) a vinyl-substituted aromatic compound, and (B) a compound selected from the group consisting of a C5-C30 olefin, a polyalkylene compound, and mixtures thereof. A mole ratio of A/B in the reaction mixture ranged from about 0.25:1 to about 5:1. The lubricating composition optionally included a minor amount of at least one non-grafted olefin copolymer, styrene-isoprene copolymer, methacrylate copolymer, or styrene butadiene copolymer with number average molecular weight greater than about 50,000 up to about 300,000.

U.S. Patent No. 6753381 claimed synthesis of olefinic polymer blends and their application as viscosity index improver with better low temperature property. The patent compared the performance of two polymer samples, a polymer blend containing a high ethylene content ethylene-propylene copolymer and a low ethylene content ethylene-propylene copolymer. The molecular weight of the polymer blends varied within 20,000 to 3,00,000 for different composition.

U.S. Patent No. 4517104 described viscosity index improver and dispersant properties of some ethylene copolymers. Ethylene copolymers, such as copolymers of ethylene and propylene; and ethylene, propylene and diolefin; etc., were reacted or grafted with ethylenically unsaturated carboxylic acid moieties, preferably maleic anhydride moieties, and reacted with polyamines having two or more primary amine groups and a carboxylic acid component, preferably alkylene polyamine and alkenyl succinic anhydride such as polyisobutenyl succinic anhydride. These reactions incorporated varnish inhibition and dispersancy into the ethylene copolymer while inhibiting cross-linking with resulting viscosity increase, haze or gelling.

U.S. Patent No. 4137185 invented some stabilized imide graft of ethylene copolymeric additives for lubricants. The oil-soluble, derivatized ethylene copolymers derived from about 2 to 98 wt. % ethylene, and one or more C<sub>3</sub> to C<sub>28</sub> alpha-olefins, e.g. propylene, which were

grafted, preferably solution-grafted under an inert atmosphere and at elevated temperatures and in the presence of a high-temperature decomposable free-radical initiator, with an ethylenically-unsaturated dicarboxylic acid material and thereafter reacted with a polyamine having at least two primary amine groups, e.g. an alkylene polyamine such as diethylene triamine, to form carboxyl-grafted polymeric imide, usually maleimide. The derivatives were then treated with an anhydride of a C<sub>1</sub>-C<sub>30</sub> hydrocarbyl substituted acid, preferably acetic anhydride, to yield an oil-soluble stable amide of said polyamine whereby oil solutions of said amide derivative were characterized by minimal viscosity change over an extended period of time. 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 described some oleaginous compositions containing novel ethylene alpha-olefin polymer as viscosity index improver additive. The ethylene alpha-olefin polymers comprising monomer units derived from ethylene and at least one alpha-olefin represented by the formula H<sub>2</sub>C=CHR<sup>1</sup> wherein R<sup>1</sup> is an alkyl group of from 1 to 18 carbon atoms, and wherein said polymer has a number average molecular weight of from above 20,000 to about 500,000, and an average of at least about 30% of the polymer chains contained terminal ethylidene unsaturation.

Depending on the type of present diene, there are styrene-butadiene (SBC) and styrene-isoprene (SIP) polymers. They have the optimized molecular weight which resists shear stresses when used in engine oils.<sup>10</sup> Styrene-isoprene copolymers have good high temperature and low temperature properties. The molecular weight of styrene-isoprene polymers lies between 50000 and 100000 g/mol.<sup>10,16</sup> They are most widely used in engine oils. They can also be used in other fields of application with more stringent requirements for shear stability, for example as tractor transmissions fluids and airplane piston engine oils.

Block copolymers of styrene and isoprene have also found commercial use as lube oil additive. Both diblock (A-B) and triblock (A-B-A) polymers, where A represents polyisoprene and B represents polystyrene have been reported. For maximum thickening efficiency a high yield of isoprene is desirable. Since the polystyrene regimes are oil insoluble over most of the relevant temperature range for engine oils, these block polymers function as associative thickeners. Thus the molecular weight of the individual molecules tend to be on the low side with the styrene block having Mw of 30,000 to 50,000 and the isoprene blocks in the range of 50,000 to 1,00,000.

SIP types of polymers are also reported to show better performance in star polymer structure. U.S. Patent No. 5460739 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. Patent 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.

U.S. Patent No. 4116917 describes certain star polymers comprising hydrogenated poly(styrene/isoprene) as effective viscosity index improvers. The inventors claimed that the polymers possessed excellent thickening efficiency at high temperature while also possessing very good low temperature viscosity characteristics. Again these polymers not only possessed much superior oxidative shear stability and permanent shear stability, they also possess significantly improved "temporary shear loss". Temporary shear loss refers to the temporary

viscosity loss at high shear stress conditions resulting from the non-Newtonian character of the polymeric VI improvers.

U.S. Patent No. 3668125 describes use of three-block copolymers as viscosity index improver. Some of the polymers structurally has hydrogenated styrene-isoprene-styrene unit. For both the monomer units viz. styrene and isoprene the active unsaturation was reduced to 50% or more. The terpolymers showed suitable low temperature viscosity property but less shear stable at high temperature. Again despite of their low molecular weights, they exhibited thickening power at 210° F.

U.S. Patent No. 3772196 analysed a combination of 2-block copolymer comprising a first polymer block of an alkenyl arene, e.g., styrene and a second essentially completely hydrogenated polymer block of isoprene and certain pour point depressants in a lubricant base stock having a viscosity index of at least 85. The compositions had excellent shear stability and could be formulated to pass a number of the ASTM and SAE engine oil performance and engine service classifications.

U.S. Patent No. 5278252 claimed a solid, cyclone-finishable polymer which did not exhibit cold flow, exhibited an unexpected balance of viscosity improving properties for oil compositions. The polymer was produced by hydrogenating a copolymer comprising a homopolymer block of isoprene connected to a copolymer block of isoprene and a monoalkenyl aromatic hydrocarbon.

U.S. Patent No. 6034042 discloses star polymers having tetra block copolymer arms of hydrogenated polyisoprene-polybutadiene-polyisoprene together with polystyrene. These polymers were described as having improved viscosity modifier and thickening properties.

Comparatively new U.S. Patent 20120101017 A1 described viscosity improver performance of hydrogenated styrene butadiene star copolymer. The study claimed that the star copolymer could be included about 3 to 25% and about 97 to 75% butadiene. The

star copolymer might further be incorporated in a lubricant additive in the amount of about 12 wt % of the star copolymer as compared to the base oil.

From the literature survey it is evident that the three main kinds of viscosity modifiers viz. Poly methacrylate (PMA), olefin copolymer (OCP) and hydrogenated styrene isoprene copolymer (SIP) are also used as thickener and known to possess eminent shear stability. Researchers have focused mainly on viscometric properties of them. But their tribological properties are not well investigated. Although they do not possess specific characters to be effective anti wear additive, they still can possess some anti wear benefit due to different structural feature. With this anticipation the author decided to investigate anti wear properties of some well known viscosity modifier.

Chapter II contains synthesis, characterization and performance evaluation of poly hexadecyl methacrylate and its two copolymers with styrene and 1-Decene as viscosity modifier, anti wear and thickening agent along with determination of shear stability. Chapter III comprises similar studies on some commercially obtained viscosity modifiers viz. PMA, OCP and SIP. Since tribological studies on viscosity modifiers are not well researched, the above investigations may lead towards a new direction in this area.

## **References**

References are given in BIBLIOGRAPHY under Chapter I of Part II (PP 215-216).