Part III

Preparation, Characterization, Viscometric Analysis, Compatibility Studies and Evaluation of Homopolymer of Decyl Acrylate and its Copolymer with Styrene along with their Blends as Lubricating Oil Additives

CHAPTER I

1.2 A BRIEF REVIEW OF THE PRESENT INVESTIGATION

In recent years, in view of the reduction of petroleum resources and environmental problems such as global warming, an improvement of fuel efficiency of automobiles which is aimed at reducing CO_2 emissions is required. A significant effect with low cost can be expected from lowering fuel consumption by lubricating oils, as compared to physical modification of the lubricated machinery. Therefore, the requirement for improving fuel efficiency by lubricating oils is growing.

Lubricating oils contain additives that help the lubricating oil to have a certain viscosity at a given temperature. In general, the viscosity of lubrication oils and fluids is inversely dependent upon temperature. When the temperature of a lubrication fluid is increased, the viscosity generally decreases, and when the temperature is decreased, the viscosity generally increases. For internal combustion engines, for example, it is desirable to have a lower viscosity at low temperatures to facilitate engine starting during cold weather and a higher viscosity at higher ambient temperatures when lubrication properties typically decline.

Lubricating oil compositions for internal combustion engines typically include polymeric additives for improving the viscosity index of the lubricating composition, that is, modifying the relationship between temperature and the viscosity of the oil composition to reduce the temperature dependence of the viscosity, to lower the "pour point" of the composition, that is, to allow the composition to remain fluid at reduced temperature, and to provide "dispersant" properties, that is, to allow sludge particles to remain suspended in the oil composition.

Accordingly, the viscosity modifier to be blended with lubricating oil which is required to have particularly excellent low-temperature properties is desired to exhibit an excellent effect of improving viscosity index and not to inhibit the function of the pour point depressant.

Polymethacrylates (PMAs) and polyacrylates (PAs) having monomeric chain length C_8 to C_{20} are characterized by a good effect with respect to the viscosity-temperature behaviour of the oils to which they are added as improvers, and when used in sufficiently high concentration they also show an outstanding protective effect against wear. Their pour-point lowering effect should also be stressed.

For a given class of polymers, with higher molecular weight and concentration, the viscosity of lubricating oil containing the PAs or PMAs is higher. However, higher molecular weight polymers exhibit a greater tendency to break down under the shear and high temperature conditions normally found in engine operation, frequently resulting in the loss of viscosity.

Another important characteristic required for a viscosity index improver is viscosity at low temperatures, which relates to the ease of engine cranking during start-up in cold climates. Homopolymer of PAs cannot exhibit a negligible viscosity contribution at low temperatures while providing a large viscosity contribution at engine operating temperatures. The high molecular weight and high concentration of PAs facilitate their power as VII but at the same time inhibit their power as PPD. Another disadvantage for PAs and PMAs is the treating costs for these products are comparatively high. This concept is to be understood as meaning the costs required for achieving a desired effect.

To overcome these problems copolymer of PAs with different olifinic and vinylic monomers (styrene, maleic anhydride, 1–decene etc.) has been introduced by many groups of inventors [1-3]. The treating costs for the copolymers are comparatively low due to incorporation of low cost olifinic and vinylic monomers. Although the copolymer performance as PPD quite satisfactorily, they performed poorly as VII. This is due to the lower molecular weight of the copolymers. To achieve the desired performance of the copolymers as VII, they must be added very high concentration in lube oil. However, the higher concentration of the copolymers adversely affects their performance as PPD. The need for higher concentration of the copolymers also makes their treating cost comparatively high.

Accordingly, in formulating lubricating oils to satisfy the varying conditions desired, it has generally been the practice to select those polymers which provide, at the lowest cost, the best overall balance of properties including viscosity index improvers (VIIs) and pour point depressants (PPDs).

The idea of combining the homopolymers and copolymers of the same class of PAs, in order thereby to produce lubricating oil additives with improved properties, was obvious. Industry awaits the preparation of lubricating oil additives in a liquid (oil-based) form and with the highest possible absolute polymer content.

It has now been found that lubricating oil additives having outstanding properties are obtained if two different polymers of different or same kind combined to form a polymer mixture or polymer blend [4-5].

Polymers to be combined in blends are generally selected to complement each other in one or more of the following properties: cost, processability, mechanical properties, chemical resistance, weatherability, flammability resistance, thermal performance and a variety of other properties. Blends are typically viewed as cost saving devices, whereby an expensive polymer may be combined with a less costly polymer to provide adequate performance at a significantly reduced price to the consumer. The blend can offer a set of properties that are not possible with either of the polymers comprising the blend.

Polymer blends may comprise miscible polymers, immiscible polymers, or a combination of miscible and immiscible polymers. Blends comprising immiscible polymers have two or more phases and such blends may be compatible or incompatible. Incompatible blends of immiscible polymers can suffer from phase separation as demonstrated by delamination or the formation of skin-core layered structures during polymer processing operations, especially injection molding. The term, "delamination," as used when referring to such materials, describes visually observed separation of a surface layer giving a flaking or onion skin effect. Incompatibility may also result in poor mechanical properties and marginal surface appearance (streaking, pearlescence, etc.). Compatible blends of immiscible polymers typically do not show any delamination and can result in acceptable end-use properties [6].

Miscible polymer blends, on the other hand, may offer desirable end-use properties and the advantage of tailoring product properties intermediate of the individual components across the miscible composition range. Miscible blends do not suffer from delamination and generally have consistent physical properties.

So while a miscible blend of two polymers is generally desirable it can be difficult to achieve. Blends of two polymers of a same or similar class might be expected to have a better chance of miscibility. However, polymers from the same class are frequently immiscible and form multiphasic compositions. Thus, polymer miscibility is difficult to predict, even within the same class of polymers.

For the foregoing reasons there remains an unmet need for non-delaminated polymer blends, i.e., blends free of delamination, which are either miscible blends or immiscible, but nonetheless compatible, blends. More particularly, there remains an unmet need to develop blends having high heat resistance, and methods of forming such polymer blends.

To achieve good mechanical properties in polymer/polymer blends, some degree of compatibility between the respective components is desirable. This may occur, even in incompatible blends that develop two separate phases, by the presence of interactions between chain segments and some degree of intermolecular mixing. By simply varying the concentration of the constituents of an incompatible blend, a compatible blend with a unique set of properties can be obtained.

Some previous work involving polymer blend additives for lube oil are enlisted below:

U.S. Patent No. 4,622,031 discloses concentrated blends of a nitrogen-containing PMA, an OCP and a "compatibilizer" graft copolymer having PMA branches grafted onto an OCP backbone, each dissolved in a hydrocarbon fluid. The compatibilizer copolymer stabilizes the thermodynamically incompatible PMA and OCP additives to discourage separation of the blend into discrete phases.

U.S. Patent No. 5,188,770 discloses a concentrated emulsion including a poly(alkyl methacrylate) copolymer and an olefin copolymer wherein alkyl methacrylate monomers are polymerized in an oil compatible liquid vehicle in the presence of an olefin polymer, hydrogenated isoprene, a hydrogenated butadiene-styrene copolymer, hydrogenated polyisoprene or hydrogenated polybutadiene.

W.O. Patent No. 2002083825 A1 is directed to lubricating oil compositions comprising polyolefins and polyacrylates. These lubricating oil compositions display good low temperature and shear performance in driveline lubricants and provide improved efficiency without sacrificing durability under severe loading conditions. The invention is also directed to polymeric compositions comprising mixtures of the polyolefins and polyacrylates.

U.S. Patent No. 4,194,057, discloses viscosity index improving compositions containing a combination of a certain class of relatively low molecular weight vinyl aromatic/conjugated diene diblock copolymers and ethylene α-olefin copolymer. The patent describes the specified class of vinyl aromatic/conjugated diene diblock copolymer as being relatively insoluble in oil and that blending with ethylene α-olefin copolymer improves solubility and allows for the formation of polymer concentrates.

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W.O. Patent No. 96/17041, discloses certain blends of star-branched styrene-isoprene polymers and ethylene α-olefin copolymers. The publication describes the addition of an amount of the ethylene α-olefin copolymer to the star-branched styrene-isoprene polymer as being effective to improve the dimensional stability of the star branched polymer so that the star branched polymer can be formed as a stable, solid bale.

In U.S. Patent No. 5,747,433, Luciani et al., discloses a composition of about 2 to about 20 percent of a hydrogenated diene/vinyl aromatic block copolymer and a selected non-ionic surface active agent, in a medium of oil of lubricating viscosity, which exhibits reduced viscosity compared with comparable compositions without the surface active agent.

E. Patent No. 1,178,102, discloses a lubricating oil composition of a lubricating base oil and a copolymer of ethylene and an α-olefin of 3 to 20 carbon atoms, having an ethylene content of 40-77% by weight and other characterizing parameters. Pour point depressants can also be present, such as copolymers of α olefins and styrene.

E. Patent No. 0,214,786 describes middle distillate additives comprising maleic anhydride and straight-chain 1-olefins, which are esterified with fatty alcohols by a polymer-analogous reaction, for improving the cold flow properties of middle distillates.

E. Patent No. 0,320,766 describes polymer blends comprising a copolymer (A1) of 10-60% by weight of vinyl acetate or a copolymer (A2) of 15-50% by weight of vinyl acetate, 0.5-20% by weight of C_6-C_{24}-alpha-olefin and 15.5-70% by weight of ethylene and a copolymer (B) of 10-90% by weight of C_6-C_{24}-alpha-olefin and 10-90% by weight of N-C_6-C_{22}-alkylmaleimide, the mixing ratio of the copolymers (A1) or (A2) to (B) being from 100:1 to 1:1. These polymer blends are used as flow improvers in middle distillates.

E. Patent No. 2154230 A1 discloses an additive composition comprising at least two viscosity index improvers containing copolymers of PMAs and PAs, and in particular to lubricant additive compositions that provide improved viscosity index properties for meeting crankcase oil performance specifications when using relatively low levels of Group III and/or Group IV base oils.

U.S. Patent No.20100120641 A1 discloses a pour point depressant for lubricants that has an effect of lowering pour points of both solvent refined base oils and high viscosity index base oils. A pour point depressant for lubricants comprising: a mixture of an alkyl(meth)acrylate polymer (A) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_A) of 12.5 to 13.8. and an alkyl(meth)acrylate polymer (B) that is composed of an alkyl(meth)acrylate containing alkyl groups having an average carbon number (C_B) of 13.9 to 15.5.

U.S. Patent No. 6,746,993 discloses a viscosity index improver defined as a polymer with a solubility parameter of 8.6-9.4, a crystallisation temperature of −15° C., or less and a steric hindrance factor of 0 to 13. The polymer comprises alkyl alkenyl ethers and C_{1-40} alkyl methacrylates, of which some may be β-branched. The viscosity index improver is suitable for gear oils, hydraulic fluids, automatic transmissions and engine oils.

U.S. Patent No. 5,763,374 discloses lubricating oil compositions containing a copolymer composed of 20-70% of alkyl acrylates and 30-80% alkyl methacrylates. The lubricating oil may be used as a gear oil or an engine lubricant.

U.S. Patent Application 2004/0077509 discloses a viscosity index improver polymer suitable for gear oils, transmissions, traction oils, hydraulic oil and engine oils. Further the polymer provides an improved shear stability and low temperature viscosity. The polymer is composed of (meth)acrylates derived from branched alcohols. The branched ester groups contain C_{18-36} alkyl groups, with the proviso that the group does not contain a methylene group containing more than 16 carbon atoms. The polymer further contains 5-90% of either a C_{8-17} alkyl (meth)acrylate or C_{18-24} alkyl (meth)acrylate; and 5-50% of a hydroxy, or amide or carboxyl containing monomer. The monomer with branched ester groups may be present at 5 to 90%, or to 70% or 20 to 60%.

U.S. Patent No. 7189682 B2 discloses a composition of the following components: an oil of lubricating viscosity; a polymethacrylate viscosity modifier; an ester of a maleic acid/styrene copolymer; and optionally, an additive package that imparts to the fluid the capacity to meet bench and dynamometer tests specified by an equipment manufacturer, is suitable for use as a functional fluid such as a tractor hydraulic fluid, under a wide variety of climatic conditions.

Thus from the above literature survey it has been observed that reports regarding the development of a multifunctional polymer blend additives comprising both VII and PPD properties are still limited. Again works involving polymer blends of the same class, particularly homopolymer of PA with its copolymer of styrene as VII and PPD for lube oil are limited and has not been thoroughly investigated before.

It is the object of the present invention to provide a lubricant oil additive which improves the viscosity index of lubricating oil compositions and also is cost effective. Another object of the present invention is to provide a lubricating oil composition which has good low temperature properties.

This work is directed to the processes for preparing the mixture, to additive concentrates and to lubricating oil compositions. The overall effect of blending a low molecular weight, low vinyl content, crystalline acrylate copolymer with a higher molecular weight, acrylate homopolymer is to produce a polymeric viscosity improver composition for lubricating oils which has good thickening efficiency at high temperatures, and good low temperature properties without the problems of gelation. The result is a viscosity improver composition of decyl acrylate homopolymer with the outstanding low temperature properties of the decyl acrylate - stryrene copolymers without the problems associated with them.