Part II

Maleic anhydride based additives - synthesis, characterization and performance evaluation as multifunctional additive for lube oil

Chapter I

Background of the present investigation

The primary function of a lubricant is to create a film barrier between the moving two engine parts to reduce friction and wear. It also acts as a coolant, suppresses harmful deposit formation, controls corrosion and oxidation. Since the base oil alone cannot meet these challenging demands, performance-enhancing additives formulations are added to the lubricant formulation. These packages can include pour point depressant (PPD), viscosity modifier (VM), antiwear, antioxidant, corrosion inhibitor, detergent and dispersant components. Not only these additives can improve overall efficiency in the engine, they also extend the lifetime of the lubricant and engine parts.[1]

In recent context multifunctional additives play the major role in the technology of engine oils. Research throughout the world is increasing to produce multifunctional additives.[2-4] Again, according to the literature, in case of multifunctional additive more than one additive performance can be found in a single system.[5, 6] Thus introduction of multifunctionality in single system has become very relevant now a days. With this background the present investigation comprises the incorporation of three major additive performances (VM and PPD or VM, PPD and dispersant or antioxidant and detergents/dispersants) in single additive system.

In the general introduction section, we have discussed in details about VM, PPD, antioxidant and detergent/dispersant. In this present investigation, we will discuss about maleic anhydride based polymeric additives and Mannich base type additives and their multifunctional activity in lube oil. In accordance with the present investigation, it will be very pertinent to include a brief review on VM, PPD, antioxidant and detergents/dispersants additives for lubricating oil. The review of the foregoing researchers regarding on multifunctional lube oil additives is being presented, in a selective manner, in the following paragraphs.

U. S. Patent No. 3087893 described the preparation of copolymers of maleic anhydride and unsaturated esters of carboxylic acid. The prepared copolymers act as a multifunctional (VM and PPD) lube oil additives. U. S. Patent No. 4514314 claimed for the preparation of copolymer of 1- olefin having carbon number C_{14} to C_{18} and maleic anhydride esterified with 1.2 to 2.0 moles of 2- alkyl alkanol having carbon number C_{32} to C_{36} per molar proportion of maleic anhydride moiety and used as a pour point depressant for lubricating oil.

U.S. Patent No. 4668412 has described the synthesis of a terpolymer of maleic anhydride and lauryl methacrylate and stearyl methacrylate which has been formulated with dimethyl amino propyl amine and Mannich base of N- amino ethyl piperazine, paraformaldehyde and 2, 6-di-

t- butyl phenol. The prepared terpolymers act as dispersant, VII and PPD for lube oil. U. S. Patent No. 4707285 has claimed the synthesis of VM, PPD and dispersant copolymers which can be prepared by solutions of ethylene – propylene copolymers grafted with vinyl containing monomers, maleic anhydride or ethylenically unsaturated acids and finally formulated with polyols, polyamines and hydroxylamine as well as hydrogenated isoprene or butadiene copolymers.

U. S. Patent No. 4089794 claimed that copolymers of ethylene and one or more α- olefin having carbon number C_3 to C_{28} are grafted under an inert atmosphere and at elevated temperature with an ethylenically unsaturated carboxylic acid in the presence of free radical initiator and finally reacted with polyamine or hydroxyl amine to form a carboxy – grafted polymeric derivatives which have good engine sludge and varnish control behaviour in lubricating oil and fuels. If molecular weight of the polymeric derivatives is above 10000, then these are useful as viscosity index improver also.

U. S. Patent No. 4292185 claimed that the polymeric additives comprising a diene – modified olefinic backbone polymer functionalized with chloro sulphonyl isocyanate and post reacted with a nitrogen compound having at least one 1^o or 2^o amino group. The additives impart detergent, VII and other useful properties to lubricating oils and motor fuels.

U. S. Patent No. 5271856 described the synthesis of novel polymers prepared by reacting with a heterocyclic nitrogen compounds containing at least one –NH- group in the ring, an aldehyde and amino substituted polymer to form an oil soluble Mannich base derivative which are useful as antioxidant additive for lubricating oils and fuels.

In 2009, Abdel- Azim et al. reported the maleic anhydride based polymeric additives as multifunctional lube oil additives. They prepared the copolymer of maleic anhydride and styrene. The copolymer was esterified separately with different alcohols (dodecyl, hexadecyl, octadecyl and docosanol) to prepare four co polymeric additives and the performance was evaluated as viscosity modifiers and pour point depressants for lube oil. Another three polymeric additives were prepared by amidation of maleic anhydride – styrene copolymer with different long chain amines (dodecyl amine, hexadecyl amine and octadecyl amine) and performance was evaluated as viscosity modifiers, pour point depressants and dispersants for lube oil. They found that efficiency as VII or VM increases with increasing the molecular weight of the prepared polymers and the aminated products have a good dispersancy for sludge and solid particles.[7] In 2011, Abdel-Azim et al. reported another similar type of work based on maleic anhydride and 1- octadecene copolymer and the copolymer was esterified

with different alcohols and aminated with different long chain amines and performance was evaluated as VM, PPD and dispersants for lube oil.[8]

In 2012, T. Du et al. had reported the synthesis of copolymers of ester of methacrylic acid and maleic anhydride at different molar ratios (1:1, 1:2, 1:3, 1:4, 2:1, 3:1, 4:1) and performance was evaluated as pour point depressant for lube oil. The best result obtained by the research group when the molar ratio was 3:1.[9] In 2015, Atta et al. reported the synthesis of copolymers of vinyl acetate and maleic anhydride at different molar ratios (1:1, 1:2 and 2:1) followed by esterification with different types of n- alkanol (dodecyl, stearyl or behenyl alcohol). The esterified product was used as PPD for crude oil. The best performance as PPD was found when the molar ratio of copolymer is 1:2 and esterified by stearyl alcohol.[10]

In 2007, T. T. Khidr reported some maleic anhydride based polymeric additives as PPD for waxy crude oil. The copolymers were prepared by α-olefin (C_8 or C_{14}) with maleic anhydride and esterified with different alcohols (dodecyl or NAFOL 1822B alcohol). The prepared esters of the copolymers with average weights in the range of 26,300 to 38,200 were found to be more effective as pour point depressants for waxy crude oil.[11] In 2011, T. T. Khidr again reported some maleic anhydride based copolymers and terpolymers to study the flow properties for paraffin gas oil.[12]

In 2009, Zhang et al. reported the synthesis of copolymers of maleic anhydride and vinyl acetate and finally copolymer was aminated with long chain amine. The aminated polymeric additive was used as cold flow improver for diesel fuel.[13] In 2014, Feng et al. had reported the synthesis of terpolymer based on alkyl acrylate, vinyl acetate and maleic anhydride in the molar ratio of 1:1:1 and the terpolymer was used as cold flow improver for diesel fuel.[14] In 2001, Aleman-Vazquez had synthesized polyalkenylsuccinimides and their detergency and dispersancy properties evaluated in an internal combustion engine. Polyalkenylsuccinimides were prepared from polyisobutene with maleic anhydride and finally treated with primary amines. They found that polyalkenylsuccinimides obtained from ethylenediamine and tetraethylenepentamine were the best detergents/dispersants additives in fuel.[15]

In 2013, Kamal et al. had reported the Mannich base type additives for lubricating oil. The additives were prepared by p- dodecyl phenol, HCHO and different polyethylene polyamines and finally the additives were modified with P_2S_5. They investigated the efficiency of the prepared additives as antioxidant and detergents/dispersants for lubricating oil. They found that the efficiency increases with increasing the number of –NH groups in the amines used.[16]

In 2008, Ahmed et al. had reported some additives based on preparation of polyisobutylene

succinic anhydride (PIBSA) and then reaction of PIBSA with different polyethylene glycol and the products were aminated with different polyamines. They investigated the efficiency of the prepared compounds as antioxidants and detergents/dispersants for lube oil. They found that the efficiency of the prepared compounds increases with increasing the number of –NH groups in the prepared compounds and by increasing the molecular weight of the polyethylene glycols.[17]

From the above literature survey, it is appeared that multifunctional lube oil additives have greater importance than those having single or dual property, and in this direction chemistry of maleic anhydride showed potential application although the study is limited with this material. Thus considering the present need and emphasis as given by the original equipment manufacturers (OEMs), it was felt necessary to undertake some maleic anhydride based polymeric additives and Mannich base type additives towards the development of efficient multifunctional lube oil additives.

References

References are given in bibliography section under Chapter I of Part II (Page No. 185 - 186).