Theses of Ph.D. dissertation

PREPARATION AND INVESTIGATION OF MOLYBDENUM CONTAINING POLYISOBUTENE-POLYSUCCINIC ACID BASED ENGINE OIL ADDITIVES

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I. Introduction, background and aims

The purpose of socio-economic changes of the today's life is to reach the so-called sustainable development by maintaining or even improving the tendency of the technical development that started 150 years ago. Perhaps the most important driving force of the progressive development has been seen during the last 100 years was the internal combustion engine (actually the engine powered automobiles), which could provide the transportation of material goods, whereto new challenges are waiting for keeping its position. These challenges promoting the professionals working in the multidisciplinary science of engine design to obtain new developments.

The never seen development of engine construction resulted in new technical discoveries like the high pressure (up to 2000 bar) direct injection systems; the continuously variable transmission; the three-way catalytic exhaust gas treatment systems; the selective catalytic reduction technique to reduce the NO_x emission; the variable and pneumatic valve timing; the intelligent engine control assemblies and so on. In parallel with this the engineering materials and manufacturing technologies have also been further developed. Titanium and magnesium alloys are used in mass production to reduce the inert mass of high speed moving engine parts; new type of vacuum and gravitational casting has come up, which can provide more brittleness despite of having less self-weight; moreover the using of different coatings (ceramic, diamond like coating, molybdenum containing surface films) is spreading recently. The two most important driving forces of these developments are the protection of the environment and the energy-efficient engine operation, in other words the reduction of fuel consumption.

The purpose of the above mentioned developments is to get more performance out of the engine with minimal fuel consumption and emission. The changing of the construction and operating parameters of the internal combustion engine requires also the development of the applied lubricants. The lubricant used in the largest volume at the lubricating regions of internal combustion engine such as the piston-cylinder system; the moving parts of the crankshaft, the camshaft and the valve stem is the engine/crankcase oil. The actual performance level specifications postulate so high requirements of the engine oils that their fulfilment is impossible by using mineral oils mixed with a small amount of functional additives. Compared to the former approach (1-2% additive content) the additive content of a modern high performance engine oil is above 25%.

The increasing specific load (thermal, oxidation, soot) of the engine oil and the prolonged oil changing periods highlighted the importance of the detergent-dispersant effect and the satisfactorily basic (neutralizing) capacity. In addition the higher long-term shear stability of additives (long-chain polymer molecules) is getting more and more important to maintain the strength of the lubricating film, as well as the development of efficient friction modifiers to reduce the fuel consumption.

During the development of new additives the effective environmental and emission regulations has to be taken into consideration. As an example, the concentration of the widely used zinc-dialkyl-dithiophosphate (ZnDDP) type antiwear and antioxidant additives in the engine oil has to be reduced, despite of their high efficiency and low price. Their sulphur content increases the SO_x emission and decreases the efficiency of the NO_x catalytic converters; their phosphorus content poisoning irreversibly the active centre of Pt and Pd containing catalytic devices. Moreover the sulphate ash originating from the combustion results the plugging of the Diesel Particulate Filters. To reduce these deteriorating effects the forthcoming engine oil performance levels specify lower sulphur, phosphorus and metal concentration. In parallel with the reduction of ZnDDP concentration the viscosity of base oils has to be also decreased to provide better fuel efficiency. But the lower viscosity base oil requires the use of more efficient antiwear and friction modifier additives.

Use of molybdenum-dithiocarbamate type additives can be a way of reducing phosphorous content. As a result of the conditions prevailing at wearing surfaces (high temperature and pressure) it is proved that a MoS_2 or MoS_x containing tribofilm forms on metal surfaces. Due to the graphite-like octahedral crystalline structure of MoS_2 it has excellent friction reducing capability. In the planar crystalline structure the layers are bounded to each other by weak Van der Waals forces and can slide to the direction of the constraining force and able to build up such a tribofilm, which is efficient in boundary lubrication. Their widespread application is constrained by the fact that the efficient operation of molybdenum-dithiocarbamate additives requires the appropriate, oxidizing reaction conditions. But the high level of oxidation can lead to the depletion of the additive content which results the premature deterioration of the friction modifying effect, since - due to their low thermal and oxidation stability - the molybdenum-dithiocarbamate additives degrade not only at the metal surfaces but also in the bulk of the oil. This kind of instability makes questionable the reality of efforts for prolongation of engine oil changing periods.

To eliminate the above mentioned drawbacks of molybdenum containing additives the purpose of our research work was to develop a new type of polyisobutene-polysuccinimide detergent-dispersant additive which has a significant additional friction reducing effect. According to our working hypothesis the prepared molybdenum complex compound will form a satisfactorily stable chemical bond with the reactive groups of polyisobutene-polysuccinimides, consequently it will be much less sensitive against oxidation and thermal effects than the molybdenum-dialkyl-dithiocarbamates. This increased stability can ensure that the molybdenum is released from the chemical structure of the dispersant only under the extreme conditions of the friction and wear processes and does not form solid sediment due to the oxidative degradation.

The main purposes of the research work were the following:

- Modification of the conventional laboratory screening methods to reach more reliable characterisation of the new higher performance level additives than that of the former methods.
- Computerised modelling of the kinetics of preparation of polyisobutene-polysuccinic-acid intermediates of polyisobutene-polysuccinimides in case of using different co-monomers and investigation of the effect of operating parameters on the product properties. (polymerisation experiments by the application of dynamic modelling strategy).
- Investigation of complex compounds formed from molybdenum-trioxide and triethanol amine in aqueous solution.
- Determination of the reaction parameters of preparation stable molybdenum containing polyisobutene-polysuccinimide additives.
- Investigation of the efficiency of molybdenum containing polyisobutene-polysuccinimides in engine oils.

II. Experimental and test methods

In the first part of our work we demonstrated that the former laboratory bench tests were not appropriate for characterisation of the newly developed additives. To be able to find the right direction of the additive development we had to modify the available bench tests in parallel with the preparation of different versions of additives.

For analytical investigation of the intermediates FTIR, NMR (^{1}H, ^{13}C, ^{95}Mo, ^{14}N and ^{17}O), XPS, XRF, TG methods were applied. The chemical structure of the additives was identified on the basis of GPC and FTNIR data. The morphology of wear surfaces was characterised by using SEM, the chemical composition of surface layers was investigated with EDAX techniques.

III. New scientific results

1. On the purpose of better characterisation of the additive efficiency the author has further developed the available former laboratory bench test methods.
    a. The author could reach appropriate differentiation ability of high temperature detergent-dispersant effect in case of high performance level (API SJ/CF-4) engine oils by the modification of the Panel Coker test.
    b. For characterisation of friction reducing effect the conventional 4-ball method has been modified. The author has developed a new measurement method that used computerised control, detection and data evaluation. By using this new method the difference of efficiency can be evaluated at 95% of confidence level of two additives with almost the similar friction reducing effect with different chemical structure.
2. The author has demonstrated that the by-product formation in the surface transport region of solid droplets of dissolving maleic anhydride is faster than the formation of the PIB[MSA, co-monomer]$_n$ grafted copolymer, which is the target product. The author has proved by using the dynamic model of terpolymerisation that by decreasing the molecular weight of α-olefin co-monomers the concentration of unwanted long-chain [MSA]-[α-olefin] heteropolymers not grafted to polyisobutene is increasing.
3. By using ^{1}H, ^{13}C, ^{95}Mo, ^{14}N and ^{17}O NMR spectroscopy, XRF, TG and IR techniques, the author has demonstrated that the MoO_3 forms octahedral molybdenum(VI) oxocomplex with the triethanol-amine in aqueous solution. The ligand triethanol-amine coordinates to the molybdenum atom with two of its hydroxyl- groups by forming an eight-membered chelate ring while the third hydroxyl-ethyl group ("arm") is free (not bounded to the molybdenum). With NOESY, EXSY measurements the author has proved that the number of bounded "arms" is statistically two, but in fact this structure is the result of a dynamic equilibrium in which the bounded and unbounded "arms" are alternating so slowly that it can be detected on NMR timescale.
4. The MoO_3 was successfully built into the chemical structure of the PIB-polysuccinimides. During the development of the additives with appropriate friction reducing and detergent-dispersant effect the following main results were obtained:
    a. It was demonstrated that the molybdenum donor compounds can not be built into the PIB-polysuccinimide structure.
    b. It was determined that the 0.4-0.6wt% molybdenum containing additive does not show opalescence and this result can be reached only by using water soluble MoO_3-triethanol-amine complex compound.
    c. It was determined the appropriate reaction conditions and component molar ratios required to build in the maximum amount of molybdenum to the chemical structure of the additive (thereby the filtration as a technological step can be eliminated) were necessary to maintain the ideal ratio of polarity/apolarity ensuring the proper oil solubility and friction reducing effect.

d. It was determined that these new additives themselves have a little friction reducing effect but used in composition with sulphur donor compounds this effect reaches the same level or even surpass that of the commercial molybdenum-dialkyl-dithiocarbamates additives with the same molybdenum content.
e. It was proved that the products of additive synthesis starting from the intermediate products - prepared either with C_{20} α-olefin or without co-monomer - had the highest friction reducing and detergent-dispersant effect.
f. It was demonstrated that the synthesis of stable additive molecular structure requires an after-treating compound with proper structure and molecular weight.
g. It was concluded that the building of sulphur-donor compounds into the molecular structure, by using the available polyisobutene derivates, can be accomplished only with the reduction of molybdenum content.

5. The efficiency and stability of experimental additives were investigated in composition with other functional additives in fully formulated commercial engine oils.
   a. It was concluded that the chemical interactions formed between molybdenum containing polyisobutene-polysuccinimides and other engine oil additives affected the friction reducing and other properties (e.g.: thermal and oxidation stability) marginally.
   b. By using the modified Panel Coker and four-ball methods for characterisation of long–term friction reducing and detergent-dispersant effect it was demonstrated that the molybdenum containing polyisobutene-polisuccinimides have the same or even better long-term friction reducing effect, but have much higher oxidation stability than the reference molybdenum-dithiocarbamates.

IV. Industrial applicability of the results

The Department of Hydrocarbon- and Coal Processing has been dealing with development of polyisobutene-succinimide based engine oil additives for more than 30 years. During this time period the additives resulted from the development work have been successfully applied in engine oils and were commercialized by the MOL Plc. The development of molybdenum containing additives are the subject-matter of this thesis is the continuation of the former co-operation with participation of the MOL LUBE Ltd. The scale up experiments are on the way now for purpose of development of a new additive technology.

V. List of publications and conference presentations

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