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INVESTIGATION OF MODIFIED PIB-SUCCINIMIDES IN LOW SAPS ENGINE OILS

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Along with the ever stricter economical, technical and mainly environmental regulations new types of low phosphorus, sulphur and metal containing multifunctional lubricant additives are required for formulating so-called low SAPS (Sulphated Ash, Phosphorus and Sulphur) engine oils. In the greatest volume dispersant additives, mainly polyisobuthylene-succinimide types are used in the formulation of engine oils. By structural modification of the dispersants with molybdenum and sulphur containing compounds advantageous complementary effects could be achieved along dispersant efficiency. Various modified PIB-polysuccinimides with complementary antifriction and antiwear (AF/AW), viscosity-index improver and enhanced detergent-dispersant properties were synthesized and investigated both in base oil and engine oil compositions. The detergent-dispersant and the high temperature deposit preventing effects, thermal- and oxidation stability, AF/AW properties and seal compatibility were studied in fully formulated, low SAPS engine oils with reduced zinc-dialkyl-dithiophosphate (ZnDDP) content. Based on the results it was found that by using suitable additive concentrations the conventional dispersant can be advantageously combined or replaced with these new additives to enhance the properties and to reduce the ZnDDP concentration level of the experimental engine oils.

Keywords: modified PIB-succinimide, low SAPS, seal compatibility, antifriction and antiwear properties.

Introduction

In the last decade environmental regulations have been the key drivers in the automotive industry. New emission standards and engine design changes lead to changes also in the performance of the lubricants. Additional new specifications are being introduced that restrict the level of sulphated ash, phosphorus and sulphur content (SAPS) to minimize the impact on the efficiency of the exhaust after treatment systems. The challenge for the lubricants industry is to provide both extended drain intervals and fuel economy while also formulating after treatment compatible engine oils. Since higher quality base oils (Group II-VI) have very low sulphur content, the main contributors of SAPS emission are the functional additives such as zinc-dialkyl-dithiophosphate (ZnDDP), detergents and friction modifiers. To meet the new emission standards and the requirements of the engine oil's performance levels, low or non phosphorus, sulphurous and metal containing additives with higher efficiency have to be developed and produced [1-4].

On the other hand, engine oil seal compatibility tests have become more important and severe in the recent engine oil performance levels (API CI-4, CJ-4; ACEA Ax/Bx, Cx, Ex; JASO DH-1 etc.). In these tests different elastomers (Standard Refrence Elastomers) are immersed into engine oils for a given time and at a given temperature. After immersion the changes of mechanical properties and cracks are determined [2, 5].

Due to the higher soot loading caused by exhaust gas recirculation (EGR), higher flame temperatures, longer drain intervals etc. engine oils are formulated with higher detergent-dispersant concentrations to maximize the soot handling. In general for a given polyisobuthylene-succinimide type ashless dispersant a higher nitrogen content gives better dispersancy and soot handling but poorer elastomer compatibility. The balance between soot handling and seal compatibility has provided lubricant formulators with significant challenges over the past ten years, especially as seal testing has become a major part of the engine oil approval process in Europe [2, 3, 5, 6].

Not only the detergent-dispersant, antiwear (AW) and antioxidant (AO) properties but also the seal compatibility must be highlighted in case of low SAPS engine oils with reduced ZnDDP content because of the well known interactions between ashless dispersant and ZnDDP which can prevent seal damages [7].

In our experimental work molybdenum and sulphur containing PIB-polysuccinimides were prepared and investigated in an SAE 10W-40 API SJ partly synthetic engine oil formula. The possibility of the totally or partly replacement of the conventional dispersant and also the reduction of ZnDDP and its impact on the properties, especially AO, AW and seal compatibility were investigated.

Experimental

Methods

During laboratory screening tests the properties of the additives and the engine oil compositions were measured by standard and proprietary methods [8, 9].

- Detergent-dispersant (DD) properties: based on centrifugation and paper chromatography; spot dispersancy.
- High temperature deposit preventing effect: modified panel coker (300 °C Al plate, 3x3 h).
- Thermal and oxidation stability: IP-48 method (200 °C, 12 h, 15 dm^3/h air).
- AF/AW properties: modified Stanhope Seta four ball equipment (600 N, 1 h).
- Seal compatibility: VW PV 3344 (S3A test-pieces from AK-6 fluoroelastomer, pre-ageing: 150 °C, 24 h; immersion: 150 °C, 168 h).

Materials

PIB-polysuccinimide (PSI) type commercial dispersant produced by MOL-LUB Ltd. was used as reference additive. Molybdenum (Mo-PSI) and molybdenum plus sulphur (MoS-PSI) containing PIB-polysuccinimides prepared in our laboratory and a commercial SAE 10W-40 API SJ/CF partly synthetic engine oil composition were used in the present research work. The main properties of the dispersants and the composition of the experimental engine oils are summarized in *Table 1* and *2*.

Table 1: Properties of the dispersants

Properties	PSI	Mo-PSI	MoS-PSI
Kin. viscosity at 100°C, mm^2/s	496.9	283.4	310.6
Diluent oil content, %	50	50	50
TBN, mg KOH/g	14.1	10.2	11.8
N content, %	1.0	0.9	0.88
Mo content (XRFS), %	0	0.3	0.37
S content (XRFS), %	0	0	0.12
3 % additive in SN-150			
VI_E	118	108	111
PDDE, % (max. 100)	82	84	89

Table 2: Composition of the experimental engine oils

Composition, %	REF	G1	G2	G3	G4	G5	G6
Base oils	balance						
Part package	4.2	4.2	4.2	4.2	4.2	4.2	4.2
PSI dispersant	10.5	5.25	5.25	-	-	2.5	2.5
Mo-PSI dispersant	-	5.25	-	10.5	-	8.0	-
MoS-PSI dispersant	-	-	5.25	-	10.5	-	8.0
ZnDDP	1.1	0.55	0.55	0.55	0.55	0.88	0.88

Results and discussion

The potential detergent-dispersant efficiency (PDDE) of the experimental engine oils was found to be high (>80%) and similar to each other, so the concentration of the experimental dispersants and ZnDDP did not alter this property *(Fig. 1)*. In case of spot dispersancy test, where the carbon black suspensions of the engine oils were treated at different temperatures with and without water, greater differences can be observed among engine oils. At higher experimental dispersant concentrations (8 and 10.5%) the efficiency slightly decreased because of their higher polarity. In case of 0.55% ZnDDP, 5.25% commercial and 5.25% modified dispersant (G1 and G2) the efficiency of the reference engine oil was achieved. In case of high temperature deposit preventing effect the low SAPS experimental engine oils were found to be analogous to the reference oil which contained 1.1% ZnDDP.

Both the thermal and oxidation stabilities are very important due to the reduced ZnDDP concentration and thus the reduced antioxidant capacity. After thermal treatment the samples with higher modified dispersant concentration showed better stability than the reference oil while G1 and G2 oils had similar results *(Fig. 2)*. After oxidation test higher changes in the viscosities could be observed but these changes did not exceed that of the reference oil. Despite reducing the ZnDDP level by 20 and 50% similar thermal and oxidation stabilities were detected in case of the engine oils with modified dispersants.

Antiwear (AW) and antifriction (AF) properties were studied by modified four-ball method in which the AF effect was characterized by the final temperature (T_{max}) achieved at the end of the test [9]. The most important conclusion of the tests that the reduction of ZnDDP did not cause additional wear problems because the complementary AF/AW effects of the modified dispersants could compensate the lower level of ZnDDP concentration. When the ratio of modified dispersant and ZnDDP was higher (G3 and G4) better AF/AW properties could be observed *(Figure 3* and *4)*. It seemed that additive competition on the metal surfaces played important role thus at higher modified dispersant/ZnDDP ratio the molybdenum containing dispersant could build up more efficient friction and wear reducing tribofilm.

The reduction of ZnDDP concentration can cause seal compatibility problems due to decreased interactions between succinimde type dispersant and ZnDDP which can cause fluoroelastomer seal damage. VW PV 3344 seal tests of the low SAPS experimental engine oils with reduced ZnDDP concentration showed no adverse effects on seal compatibility *(Table 3)* even if the conventional dispersant was completely replaced by modified ones (G3, G4). Its reason could be their lower TBN and higher polarity which could easily interact with the other additives and thus the seal damaging basic amino-groups were blocked.

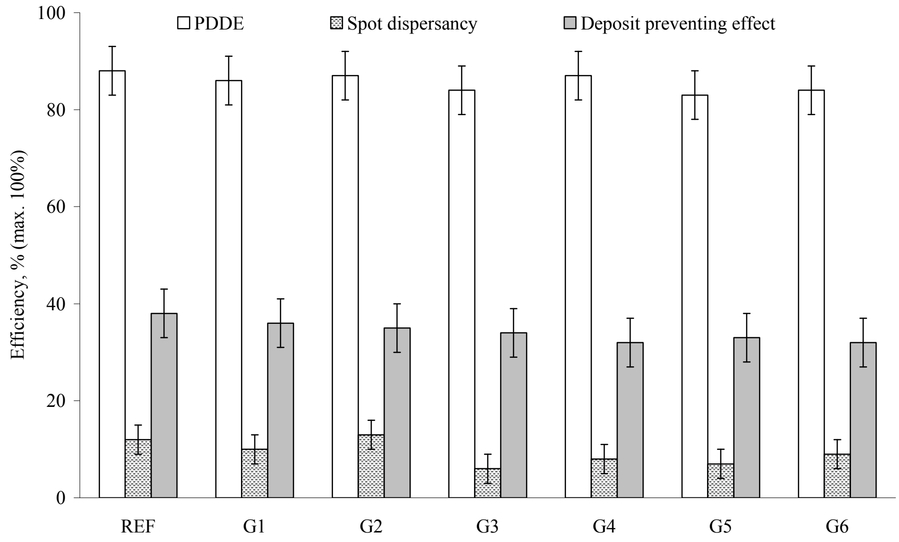

Figure 1: DD and high temperature deposit preventing effects of the experimental engine oils

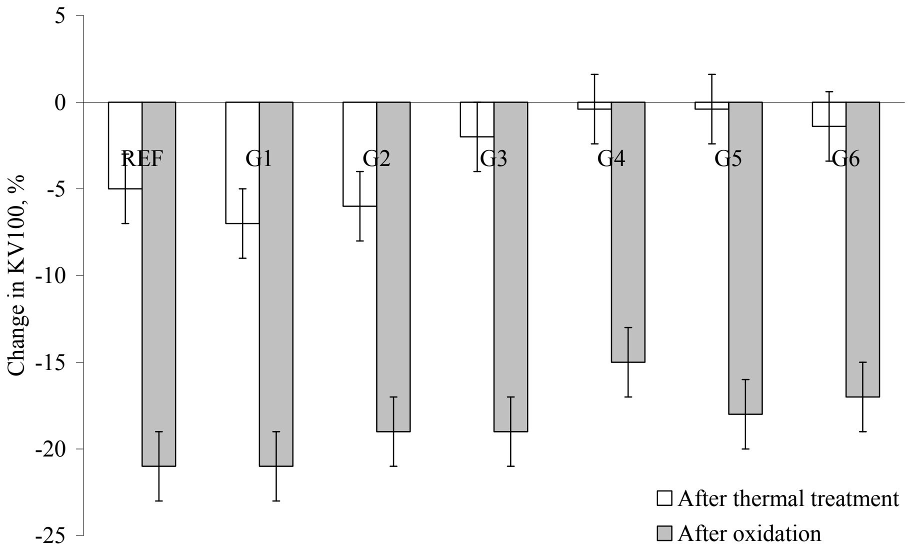

Figure 2: Thermal and oxidation stability of the experimental engine oils

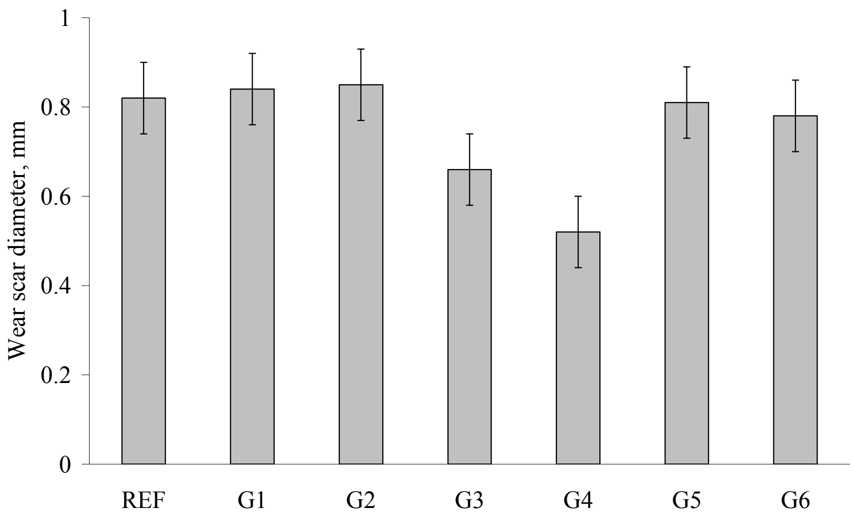

Figure 3: Antiwear properties of the experimental engine oils

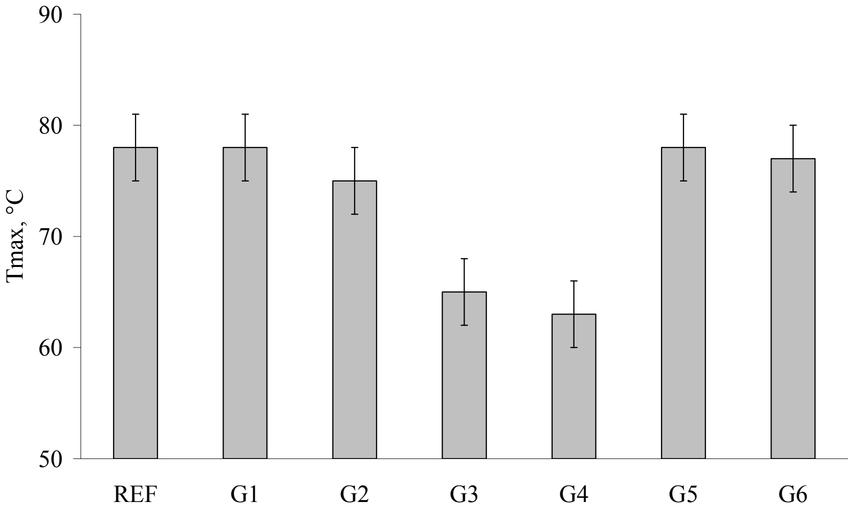

Figure 4: Antifriction properties of the experimental engine oils

Table 3: Results of the VW PV 3344 seal compatibility tests

Properties	S3A*	REF	G1	G2	G3	G4	G5	G6	Test limits
Tensile strength, MPa	15.5	10.5	11.7	12.1	12.5	12.8	13.2	13.5	≥7
Change in tensile strength, %	-	-32	-25	-22	-19	-17	-15	-13	≥-60
Elongation at break, %	395	248	285	291	312	321	328	345	≥160
Change in elongation at break, %	-	-37	-28	-26	-21	-18	-17	-14	≥-50
Hardness change (Shore A), points	70.2**	-3	-2	-2	-2	-2	-1	-1	-
Surface cracks	no	no	no	no	no	no	no	no	no

* Original S3A test-piece (without pre-ageing and immersion), ** Shore A hardness, not the hardness change

Conclusions

Modified PIB-polysuccinimide type dispersants containing molybdenum and molybdenum plus sulphur were investigated in fully formulated low SAPS (0.55 and 0.88% ZnDDP content) engine oils. Based on the results of the laboratory screening tests it was found:

- detergent-dispersant properties and the high temperature deposit preventing effect did not decrease,
- thermal and oxidation stability were unaffected despite reduced ZnDDP content,
- complementary AF/AW effects of the modified dispersants could compensate the reduction of ZnDDP,
- low SAPS experimental engine oils passed the VW PV 3344 seal compatibility test.

In this way it can be supposed but should be proved by engine tests that the modified dispersants may open up an opportunity for formulating low SAPS engine oils with reduced ZnDDP content.

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