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INVESTIGATION OF PIB-SUCCINIMIDES IN ENGINE OILS

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Along with the ever stricter economical, technical and mainly environmental regulations new types of low phosphorous, sulphurous and metal containing multifunctional engine oil additives are required. Most commonly dispersant additives, mainly polyisobuthylene-succinimides are used in the formulation of engine oils. By structure modification advantageous complementary effects could be achieved along the high detergent-dispersant efficiency. In view of this different modified PIB-polysuccinimides with complementary AF/AW, viscosity-index improver and enhanced detergent-dispersant properties were synthesized and investigated in base oil and engine oils. The potential detergent-dispersant efficiency, spot dispersancy, thermal- and oxidation stability, deposit preventing effect and AF/AW properties were studied in fully formulated engine oils. 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 of the experimental engine oils.

Key words: modified PIB-polysuccinimide, detergent-dispersant properties, AF/AW effects, thermal pre-treatment.

1. Introduction

In the last decade the environmental regulations have been the key drivers in the automotive industry. Since 2005 the maximal sulphur content of fuels has been *50 ppm* but regionally *10 ppm* fuels have to be available in the EU. Additionally attention has also been focused on the sulphur content of engine oils (Gligorijevic and Jevtic, 2004; Hancsók *et al*., 2005). New emission standards and resulting engine design changes lead to changes also in the performance of lubricants. Nowadays the Euro IV standard is leading one of the most significant changes in lubricant quality since the start of Euro emission targets. Additional new specifications are being introduced that restrict the level of sulphated ash, phosphorous and sulphur content (SAPS) to minimize the impact on the efficiency of 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 lubricants (Biggin, 2004; Otterholm, 2004). The need for the so called low SAPS oils is still increasing. The main contributors of SAPS emission are the functional additives such as ZnDDP, detergents and friction modifiers. To meet the new emission standards low or non phosphorous, sulphurous and metal containing additives have to be produced. In our latest work effective molybdenum containing PIB-polysuccinimides were prepared and investigated (Bartha *et al*., 2004; Kocsis *et al*., 2004). In the present work a new low molybdenum and sulphur containing PIB-polysuccinimide type dispersant additives were studied in two engine oil compositions. The possibility of the total or partial replacement of the conventional dispersant and also the possibility of the reduction of ZnDDP were investigated.

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2. Methods

The main properties of the additives and the engine oil compositions were measured with standard methods (viscosity, viscosity-index, total base number (TBN) and nitrogen content) and various laboratory screening tests. Molybdenum and sulphur content of the additives were determinated with EDXRFS technique. The detergent-dispersant properties were tested by a local screening method based on a centrifugation, a paper chromatography (Kis *et al*., 2003) and a spot dispersancy method. Thermal and oxidation stability of the engine oils were measured by IP-48 method. The high temperature deposit preventing the effect of the experimental engine oils were tested by a modified panel coking method Kis *et al*. (2003). The AF/AW properties were investigated by modified Stanhope Seta four ball equipment. AW properties, such as wear scar diameter (WSD), were characterized according to ASTM D2783-88 standard (Bubálik *et al*., 2004).

3. Materials

A paraffinic base oil (SN-150) produced by MOL Plc and two commercial engine oil compositions were used to test the additives. One of them was an SAE 15W-40 API CG-4 Diesel engine oil and the other was an SAE 10W-40 API SJ/CF part synthetic oil for gasoline engines. A PIB-polysuccinimide type commercial dispersant produced by MOL-LUB Ltd was used as a reference additive.

4. Results and discussion

In the first stage the properties of the individual additives were investigated. The modifications of the polysuccinimide structure resulted in lower viscosities and TBN values (Tab.1). It was concluded that by using molybdenum and sulphur containing reagents in the synthesis of the polysuccinimide structure lower values in viscosities and TBN were achieved. It was preferably caused by the higher level of acidic neutralization and by the less cross linking obtained in the additive preparation.

Table 1. Properties of the dispersants.

Properties	Commercial	Mo-PSI	MoS-PSI
$KV_{100°C}$, mm^2/s	*496.9*	*283.4*	*310.6*
TBN, mg KOH/g	*14.1*	*10.2*	*11.8*
Diluent oil, % w/w	*50*	*50*	*50*
N content, %w/w	*1.0*	*0.9*	*0.88*
TBN/N ratio	*14.1*	*11.3*	*13.4*
Mo content, %w/w	*0*	*0.3*	*0.37*
S content, %w/w	*0*	*0*	*0.12*
3 % additive in SN-150			
DI, % (max. 100)	*100*	*100*	*100*
M, mm (max. 125)	*85*	*90*	*100*
PDDE, % (max. 100)	*82*	*84*	*89*

Table 2. Composition of the experimental engine oils and their properties.

Sample name	REF SD	SD-1	SD-2	SD-3	REF DM	DM-1	DM-2	DM-3	DM-4
Composition, %w/w	Diesel engine oils				Gasoline engine oils				
Base oil	*81.38*	*81.38*	*81.38*	*81.38*	*84.5*	*84.5*	*84.5*	*85.0*	*85.0*
Part package 1	*7.12*	*7.12*	*7.12*	*7.12*	-	-	-	-	-
Part package 2	-	-	-	-	*7.0*	*7.0*	*7.0*	*7.0*	*7.0*
*Commercial dispersant**	*10.5*	-	*5.25*	*7.87*	*7.5*	-	*3*	-	*3*
*MoS-PSI dispersant**	-	*10.5*	*5.25*	*2.63*	-	*7.5*	*4.5*	*7.5*	*4.5*
ZnDDP	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*0.5*	*0.5*
$KV_{40°C}$, mm^2/s	*115.8*	*101.9*	*108.8*	*112.6*	*88.1*	*77.8*	*85.8*	*83.6*	*85.4*
$KV_{100°C}$, mm^2/s	*16.2*	*14.5*	*15.5*	*15.8*	*15.8*	*12.7*	*13.2*	*13.0*	*13.4*
$V.I._E$	*151*	*146*	*150*	*149*	*149*	*163*	*155*	*156*	*159*

* contains *50%* diluent oil

The experimental additives solved in SN-150 base oil in *3.0 w/w%* showed similar DD properties as the commercial dispersant. Thus it was found that despite the modifications the main effects were not probably decreased. It was proved also by few differences between the Potential DD Efficiency of the engine oils obtained by centrifugation and paper chromatography tests of their carbon black suspension (Fig.1). The PDDE values of the oils were high enough (above *80%*) and similar to each other. Using the spot dispersancy test considerable differences were proved between the two engine oil compositions (Fig.2). In the Diesel oils there was an increase in relative dispersancy with the concentration of commercial dispersants. It was found that in the case of the strongly polar MoS-PSI additive the dispersancy of the reference oil could be achieved only in combination of higher concentration of commercial dispersant. The experimental gasoline engine oils including the reference oil showed very low relative dispersancy (about *10%*) but the tendency of the results was the same. Reducing the concentration of ZnDDP (DM-3 and DM-4) the activity did not change significantly.

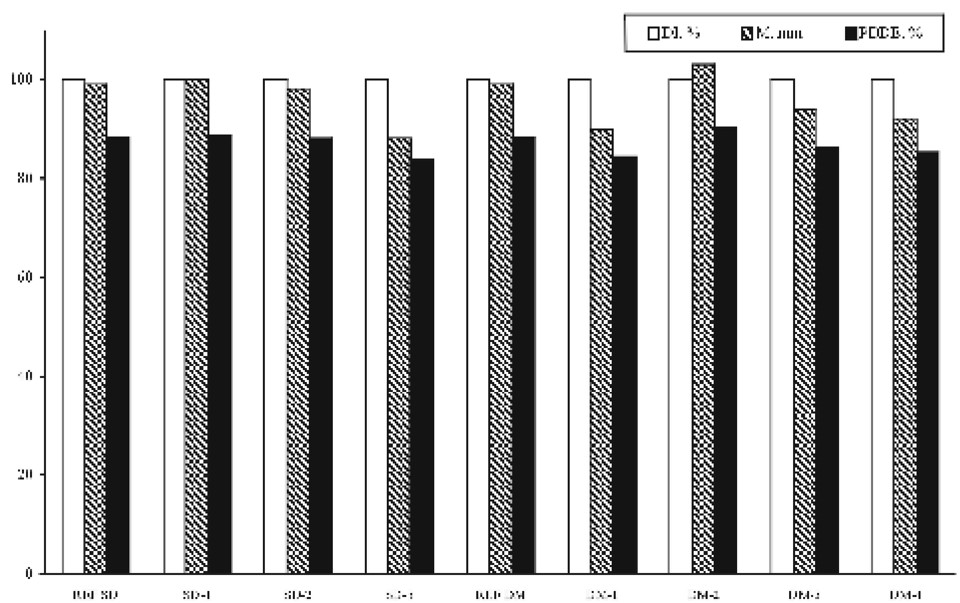

Fig.1. PDDE values of the engine oils.

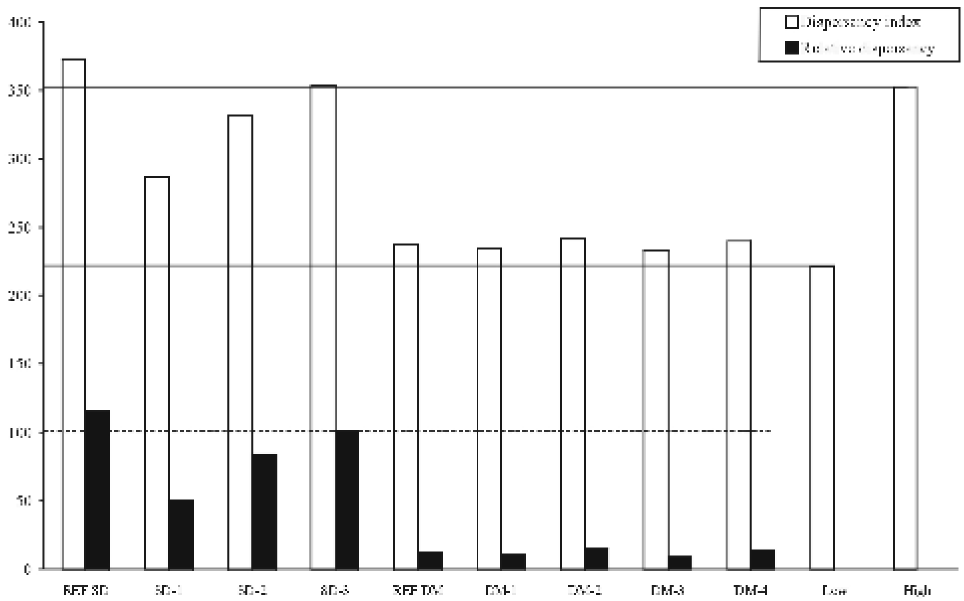

Fig.2. Spot dispersancy results of the engine oils.

The high temperature Deposit Preventing Effect (DPE) was tested with the panel coking method (Fig.3). The effects of the experimental Diesel oils were decreased at low MoS-PSI concentration. It was concluded that at high temperature advantageous interactions among the molybdenum and sulphur containing dispersant and the other additives took place as it was discussed also in our previous paper (Kocsis *et al.*, 2004). In the case of gasoline engine oils the DPE of DM-4 oil sample, with reduced ZnDDP level and combination of dispersants, could be enhanced to the DPE level of the reference oil. It was assumed that the interaction between the dispersant and ZnDDP could be reduced and thereby the DPE could be improved. Excluding DM-4 lower DPEs could be observed than those of the reference oils.

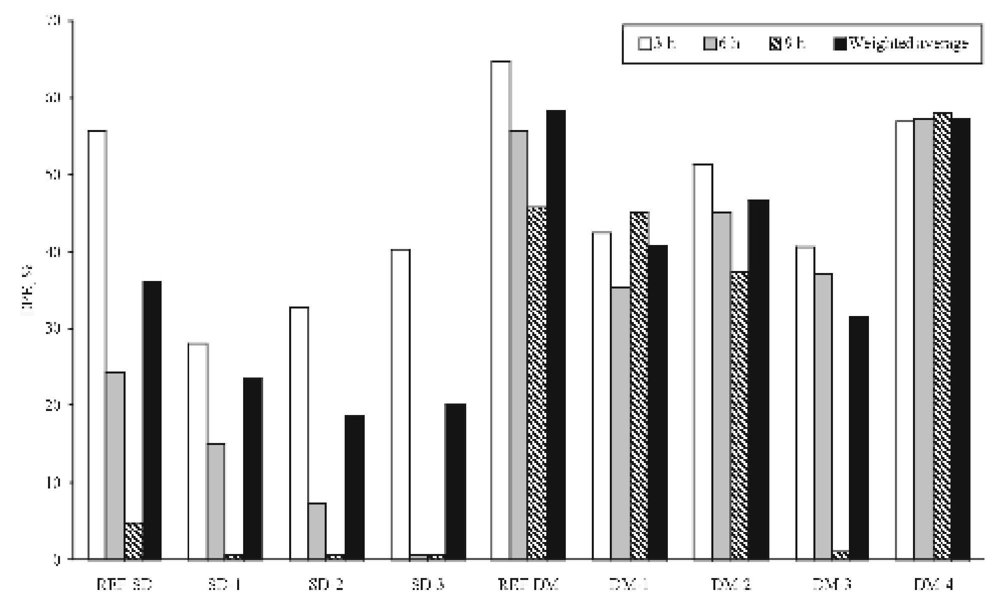

Fig.3. Deposit preventing effect of the engine oils.

The changes in the viscosities of the engine oils after thermal stability tests can be seen in Fig.4. After thermal and oxidation treatment small changes in viscosities are generally known to be advantageous. In the case of Diesel oils a significant increase in viscosities could be noticed and viscosity increase of the reference oil was exceeded by each experimental oils. A diminishing tendency of this association effects was observed with decreasing the MoS-PSI concentration. In contrast with this a small decrease in viscosities was observed in gasoline engine oils and the experimental oils were proved to be similar to the reference oil. At a lower concentration of ZnDDP less change was obtained due to the previously mentioned interactions. Viscosities after the oxidation stability test are illustrated in Fig.5. In every case a significant decrease in viscosities was observed. It was assumed that associations caused by additive-additive interactions were decomposed. In contrast with the thermal treatment decreasing the MoS-PSI concentration the change in viscosities was increased in Diesel oils. It was confirmed that the MoS-PSI had also a significant antioxidant effect. SD-1 and SD-2 oils were found to be more advantageous than the reference. Oxidation stability of the experimental gasoline engine oils was almost similar or better than that of the reference. It should be noticed that the effect of the reduced ZnDDP concentration was negligible. Its reason could be the plus antioxidant effect of MoS-PSI dispersant.

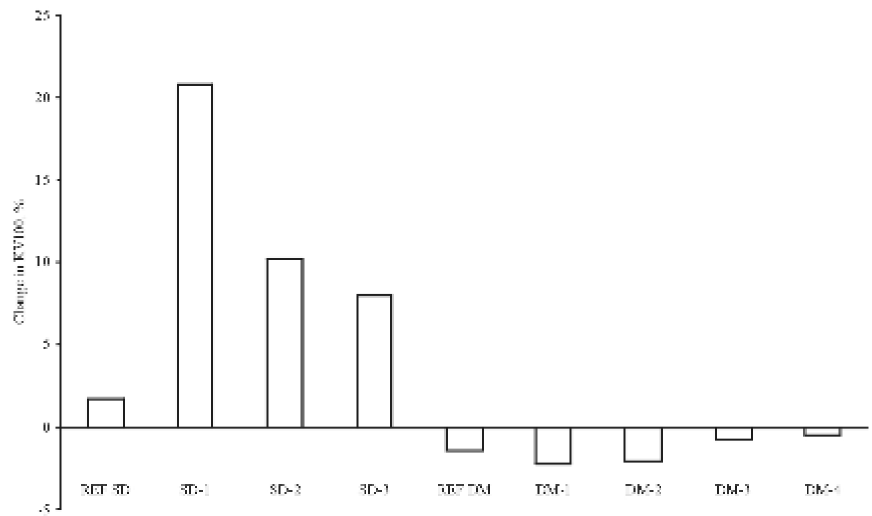

Fig.4. Thermal stability of engine oils.

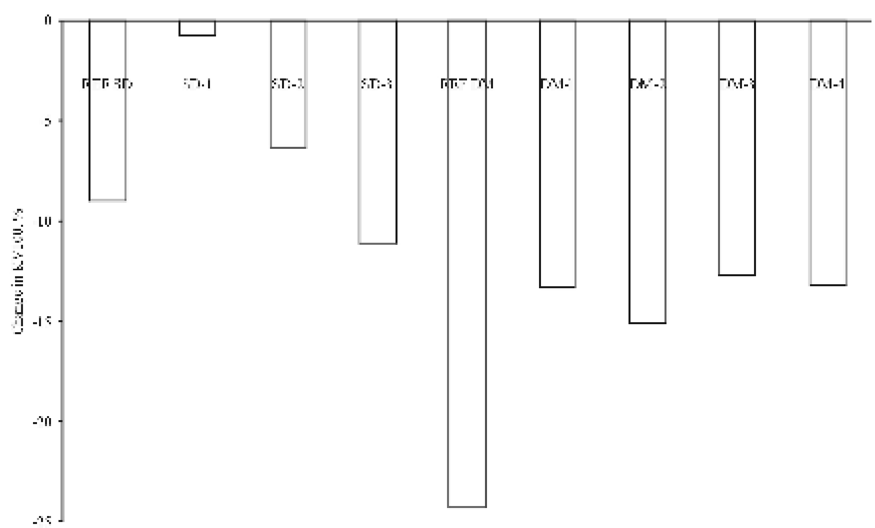

Fig.5. Oxidation stability of engine oils.

AF/AW effects of the experimental engine oils before and after thermal treatment were studied with the modified Stanhope Seta four ball method. The data can be compared in Fig.6. In the case of Diesel oils the AW effect was similar to the reference and after thermal treatment the reference and SD-1 oils were not altered. In the combinations of the commercial and MoS-PSI dispersants (SD-2 and SD-3) the WSD values were significantly increased. In the case of only MoS-PSI containing composition (SD-1) the AF effect, characterized by the final temperature (Tmax), were found to be better than that of the reference. However, in each case it could be improved with thermal treatment. The AW efficiency of gasoline engine oils was similar to the reference but after their thermal treatment the AW effect was increased while in the case of the reference oil a significant decrease was observed. The reduction of ZnDDP concentration did not result in an increase in wear. Excluding the low level of ZnDDP and MoS-PSI (DM-4) the AF efficiencies were found to be more advantageous than that of the reference. The AF properties could be significantly improved by the thermal treatment as in Diesel oils.

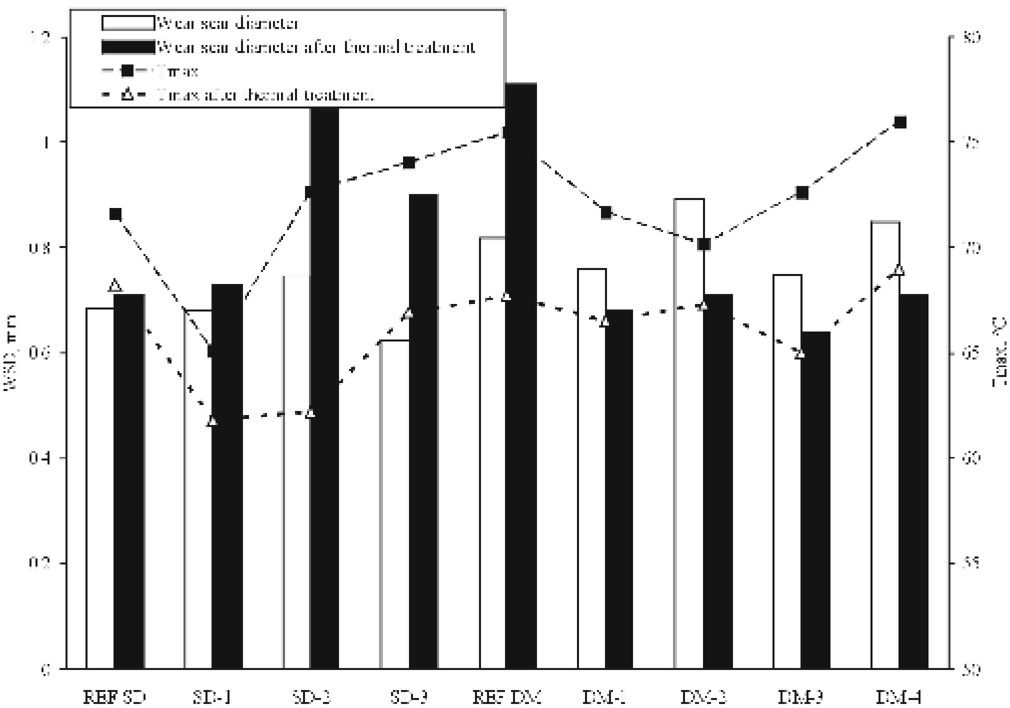

Fig.6. The AF/AW effects of engine oils before and after thermal treatment.

5. Conclusions

A molybdenum and sulphur containing PIB-polysuccinimide (MoS-PSI) type dispersant additive was investigated in two engine oil compositions. In our investigations the followings was established.

- The basic function, the detergent-dispersant effects were strongly depended on the composition and the type of the package.
- Using the combinations of the conventional and the molybdenum and sulphur containing PIB-polysuccinimides the properties of the reference packages could be achieved.
- The experimental dispersant had a significant antioxidant effect.
- A thermal pre-treatment was proved to be advantageous to the AF/AW efficiency of the experimental engine oils.

Based upon the data it could be supposed that by using the new molybdenum and sulphur containing dispersant additive the ZnDDP level could be reduced in engine oils. This may open up an opportunity for formulating environmental compatible engine oils.

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