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POSSIBILITIES OF THE APPLICATION OF POLYISOBUTENYL SUCCINIC ANHYDRIDE DERIVATIVES OF VARIOUS MOLECULAR STRUCTURES

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Detergent-dispersant (DD) effect is one of the most important properties of lubricants and fuels. To ensure these properties various types of additives are used in increasing amount in the performance additive packages. Among them ashless types and mostly polyalkenyl succinic anhydride derivatives are applied in high volumes. In this paper the main advantages of the ashless additives are presented showing the dependence of their properties on the molecule structure (monosuccinimides, bissuccinimides, mixtures thereof and polysuccinimide). Additionally, the interactions with other additives are shown which can determine the main tribological properties of the lubricants.

Keywords: ashless dispersants, detergents, polyisobutenyl succinic anhydride derivatives, interactions of additives

Introduction

The first innovations about polyalkenyl succinic anhydride derivatives, used as ashless DD additives in engine oils, were published in the 60's. Since, more than thousand patents have dealt with the alternatives of these additives and their syntheses. A wide group of them: the polyalkenyl succinimides and their derivatives are mainly used in engine oils and in fuels as detergent-dispersant additives. A classification of polyalkenyl succinimides of various molecular structures, based on their polyalkenyl chain, is the following:

Polyisobutylene (PIB) based

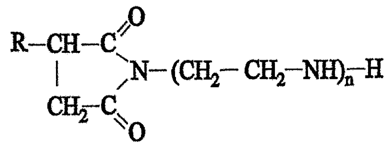
- monosuccinimides,
- bissuccinimides,
- high molecular weight succinimides (Mn_{PIB}>1000),
- modified versions of the aboves,
- ester, amide and imide derivatives of succinic acid,
- polysuccinimides based on
  - maleic anhydride (MA) – polyisobutylene copolymer [1]
  - MA – PIB – α-olefin terpolymer [2]
  - MA – comonomer copolymer grafted on PIB [3].

α-olefin copolymer based

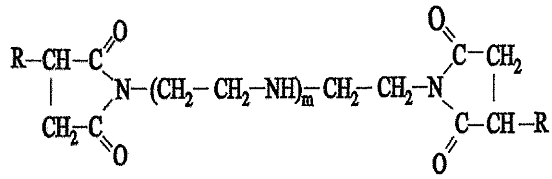
- Ethylene – propylene copolymer based succinimides [4] and other succinic anhydride derivatives
- ethylene – MA – α-olefin terpolymer [5] based succinimides
- MA – methyl methacrylate copolymer grafted on ethylene – propylene copolymer [6].

In this paper the PIB based succinic anhydride derivatives are presented. The first step of the synthesis of polyisobutenyl succinimides is usually the production of polyisobutenyl succinic anhydride (PIBSA or PIBBSA depending on the number of succinic anhydride groups in one PIB chain). The synthesis can be carried out in different ways, initiating the process thermally, catalytically or radically. The quality of the PIB used for the synthesis (the percentage of terminal double bonds, average molecular weights etc.), the technological parameters, the active material content and the molecular structure of intermediate product can be different. These factors basically determine the molecular structure and performance of the end products in engine oils and fuels. The main types of the developed and studied polyisobutenyl succinimides are shown in *Fig.1*.

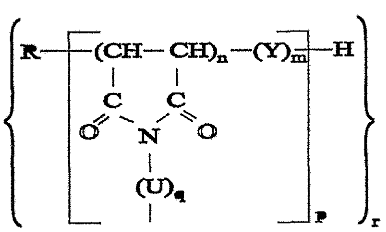
New engine designs require high quality lubricating oils in order to maximally utilise their economical benefits in fuel efficiency (reduced consumption), in longer drain intervals and in lower emissions. Therefore the understanding of the properties and interactions of the additives working together in lubricating oils is of increasing importance.



Polyisobutenyl monosuccinimide (MSI)



Polyisobutenyl bisuccinimide (BSI)



General molecule structure of the polysuccinimide (PSI)

Where: **MSI, BSI:** R=polyisobutenyl group (M_n= 300-30000); n, m $\geq$ 1 (integer);

PSI: R= polyolefin chain; U= $-CH_2-CH_2-(NH-CH_2-CH_2-)_x$; n,p,g,r $\geq$ 1; Y= bifunctional hydrocarbon chain; x, m $\geq$ 0.

Fig.1 Polyisobutenyl succinimides

Table 1 The properties of the synthesised polyisobutenyl succinimides

Type of additive	MSI	MBSI*	BSI	PSI
PIB molecular weight	1000	1000	1000	2300
Kinematic viscosity at 100 °C, mm^2/s	230	70	50	510
TBN, mgKOH/g	82	44	26	19
Nitrogen content,%m/m	3.2	1.7	1.3	1.0
Base oil content,%m/m	45	45	45	45

* Blend of mono-and bissucinimide

Table 2 DD effects of performance additive blends

	Washing efficiency (WE)	Detergent Index (DI)	PDDE
MSI+ZnDDP	0	--	0
+ Ca-salycilate	0	--	0
+Ca-phenate	0	---	0
+Ca-sulphonate	++	---	+
MBSI+ZnDDP	0	0	0
+ Ca-salycilate	0	0	0
+Ca-phenate	0	0	0
+Ca-sulphonate	++	0	+
BSI+ZnDDP	0	-	0
+ Ca-salycilate	+	--	+
+Ca-phenate	0	--	0
+Ca-sulphonate	+++	0	+++
PSI+ZnDDP	++	---	0
+ Ca-salycilate	+++	-	++
+Ca-phenate	+++	-	++
+Ca-sulphonate	+++	-	++

---...0...+++ : Strength of significance

Experimental

The interactions between performance additives were studied extensively [7]. The studies showed that the interactions are able to modify DD, extreme pressure and antiwear (EP/AW) properties of individual additives. In order to examine the ability of interaction of the developed additives', polyisobutenyl succinimides were synthesised having the main properties listed in *Table 1*. To investigate the properties of these succinimides in various mixtures containing performance additive, the blends represented in *Table 2* were prepared (dispersant content 3.5%m/m as active material, detergents 5.0%m/m and ZnDDP 1.0%m/m). The DD effects were examined by using the testing methods of washing efficiency (WE), detergent index (DI) and potential-detergent-dispersant-efficiency (PDDE) [8].

The data of *Table 2* represent that interactions between performance additives enhance the WE significantly in mixtures of BSI and calcium sulphonate. All blends show unchanged or increased PDDE values. Other important measurements were done to determine the rheological properties (change of relative viscosity and of viscosity index) which results are characterised by *Figs.2* and *3*. These show the strength of interactions between detergent additives and succinimide dispersants regarding rheological properties which is in the order of calcium salicylate > calcium phenate > calcium sulphonate. The polysuccinimide shows the most significant VI increasing effect with calcium salicylate. In order to examine another very important effect of the interactions of these additives, polysuccinimide was used for measuring the changes of EP/AW property of the additive blends. *Table 3* contains the main results of the standardised four ball tests (ASTM D 2783).

As it can be seen in *Table 3*, polysuccinimide itself has EP/AW effect and the best result was obtained when calcium salicylate or calcium phenate was used together with polysuccinimide and ZnDDP additive.

Taking into consideration the presented results, the synergy of the additives can be utilised in the formulation of engine oil compositions of high performance level with polysuccinimide, utilising its outstanding DD, viscosity and viscosity index improving and EP/AW effect whilst reducing the cost of formulation by reducing the conventionally required amount of rheological and EP/AW additives. The formulation [9] meets the requirements of API SJ/CF, ACEA A-3/98, CCMC G5/CD2 and other OEM's (Ford, GM, Rover) specifications.

Summary

Various types of polyisobutenyl succinimides were examined regarding their properties and the effects of

Table 3 Data of four ball tests of different additive blends

Load,N	Base oil SN-150	+ PSI	+PSI+ ZnDDP	+PSI+ZnDDP+Ca-salicilate	+PSI+ZnDDP+ Ca-phenate	+PSI+ZnDDP+ Ca-sulphonate
	Scar diameter, mm					
600	1.965	1.941	-	-	-	-
800	2.637	2.398	0.341	0.312	0.311	0.312
1000	2.800	2.564	0.735	0.728	0.394	0.379
1260	Welding	3.186	2.278	2.106	2.047	2.226
1400		Welding	2.413	2.294	2.275	2.240
2000			2.611	2.605	2.630	Welding
2400			Welding	Welding	Welding	

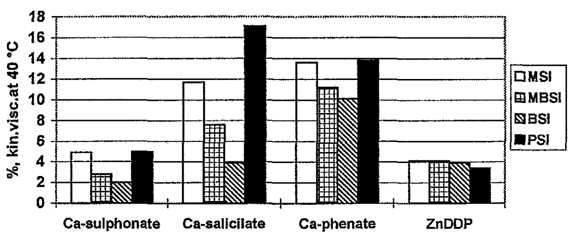


Fig.2 Relative changes of kinematic viscosity at 40 °C by the interactions of the additives

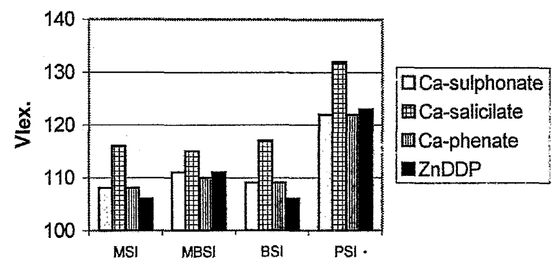


Fig.3 Changes of viscosityindexes (VIex) of the additive blends

interactions, blended with performance additives of lubricating oils. Detergent-dispersant, extreme pressure/antiwear and rheological properties were shown which demonstrate that utilising the synergy among the additives, lubricants of the highest performance level can be formulated and the costs of formulation can be reduced.

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