Development of Multifunctional Detergent-Dispersant Additives Based on Fatty Acid Methyl Ester for Diesel and Biodiesel Fuel

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1. Introduction

Nowadays fuel blending components produced from renewable sources (biodiesel, mixture of iso- and normal-paraffins produced from triglycerides, gasoline and diesel produced from synthesis gas etc.) are an important part of the blending pool (Hancsók et al., 2007; Krár et al., 2010a, 2010b). The use of fuels produced from renewable resources is supported by several EU directives (2003/30/EC (Biofuels), 2009/28/EC (Renewable Energy Directive) and 2009/30/EC (Fuel Quality Directive).

The biocomponents of diesel fuel are mainly fatty acid methyl ester (biodiesel), produced from the catalytic transesterification of vegetable oils. Their blending is allowed up to 7% by the EN 590:2009 diesel fuel standard. The application of biodiesels causes several problems due to their properties which are different from that of the fossil diesel fuel: higher cold filter plugging point (CFPP), higher viscosity, hydrolysis (corrosion), storage stability problems, lower energy content etc. As a result new challenges rose to ensure the high quality of diesel fuel and the proper function of the engine by applying high performance additives in the diesel fuel and engine oil (Beck et al., 2010; Bubálik et al., 2005).

2. Modern diesel fuel additives

Modern diesel fuels are blended from high quality blending components and high performance additives. The additives are usually synthetic materials applied in low concentration which improve the properties of diesel fuel or provide them new, advantageous ones (Hancsók et al., 1999a; Haycock & Thatcher, 2004).

By the introduction of ultra low sulfur diesel and biofuels (e.g.: fatty acid methyl ester) into the market the importance of fuel additives increased. Among the fuel additives detergent-dispersants, lubricity improvers and corrosion inhibitors there are long chained hydrocarbon molecules with a polar head. All these three types of additives provide their effect by linking to the metal surface, as a result these additives compete for the metal surface and not all of them can reach it and provide its effect. Therefore, the development of a multifunctional additive providing two or three of the previously mentioned effects is an important research field. In the current publication the mechanism of detergent-dispersants, lubricity improvers and corrosion inhibitor additives are detailed, followed by the results of the research work.

2.1 Detergent-dispersant additives

Among the different types of additives the detergent-dispersants (hereinafter: DD) have high importance. Their share in the total additive market is about 40-50%. Their role is to clean and keep clean the fuel supply system and the combustion chamber: remove deposits and prevent their formation (Figure 1 and 2) in order to ensure the proper function of the engine (Hancsók, 1999a; Haycock & Thatcher, 2004).

Without DD additive   With DD additive   Improper fuel injection   Proper fuel injection
                                                   caused by deposits   (without deposits)
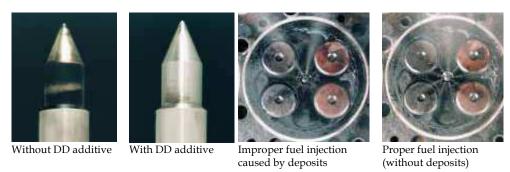
Fig. 1. Deposits on the injector   Fig. 2. Effect of DD additives on the fuel injection

Several additive types were developed for the above mentioned purpose. These additives usually have different efficiency and they have only the detergent-dispersant function. The development and application timeline of DD additives are shown in Figure 3 (Hancsók, 1999a).
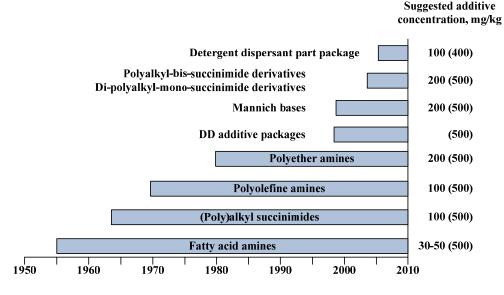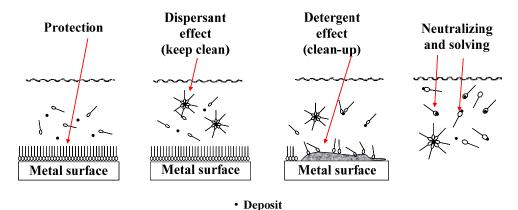

Fig. 3. Timeline of the development of detergent additives

Alkenyl-succinimides were applied as dispersants in lubricants already at the end of the '50s, in fuels in the early '60s. These were the second generation of the deposit control additives. In the '70s fuel consumption increased world-wide, as a result olefins were blended in a higher concentration. The fuel quality change and the higher olefin content resulted in lower fuel stability, and as a consequence there was a need for higher performance additives. In this period the application of polyolefin-amines started as new, high performance deposit preventing additives, followed by the application of polyether-amines, then Mannich-bases. In the latest decades the environmental and quality prescriptions towards fuels have become stricter. Nowadays, different types of polyisobutylene-mono- and bis-succinimide additives (Figure 4), polyisobutylene-amines, Mannich bases, polyether amines and their mixtures are applied in fuels (Hancsók, 1999a; Haycock & Thatcher, 2004). The application of the so-called detergent-dispersant packages containing the mixture of different, unique additives is becoming more and more wide-spread, too (Hancsók, 1999a).

PIB-mono-succinimide   PIB-bis-succinimide

Where R: polyolefin having Mn = 500-6000 average molecular weight, advantageously polyisobutylene chain
m, n: 1-5 whole number

Fig. 4. General structure of polyisobutylene mono- and bis-succinimides

The mechanism of detergent-dispersant additives is summarized in Figure 5. The additive molecules bond to the metal surface by chemisorption and prevent the formation of deposits by covering the surface. They remove deposits by their detergent action and keep in

· Deposit
∘— Detergent-dispersant additive

Fig. 5. Mechanism of detergent-dispersant additives

dispersion the insolubiles by absorbing to the impurities with their polar head. In such a way they prevent the formation of bigger agglomerates by steric hinder. They form a micellar colloid structure with the impurities, into this structure further impurities can enter by electrostatic or hydrogen bond, in this way the size of the micelle increases. As a result the additive prevents the deposits of polar compounds. Their other important function is the acid neutralization with their base group (Beck et al., 2010).

The application of detergent-dispersant additives provides several advantages for the end-users, such as (Caprotti et al., 2007; Hancsók et al., 1997; Haycock & Thatcher, 2004; Kocsis et al., 2001; Rang & Kann, 2003; Ullmann et al., 2009):

- Smooth fuel injection (preventing deposit formation)
- Smoother pressure increase during injection resulting in quieter motor function
- Better combustion
- Higher performance
- Better driveability
- Lower fuel consumption and lower maintenance costs
- Lower emission

The latest environmental prescriptions can only be satisfied by applying high performance detergent-dispersant additives. These additives are not only responsible for cleaning and keeping clean the fuel supply system and the combustion chamber, but for ensuring lower fuel consumption as well (Beck et al., 2009a; Caprotti et al., 2007; Rang & Kann, 2003; Ullmann et al., 2009).

The most widely applied DD additives are the succinimide type additives, which are mostly produced in two steps by thermal technology (Mach & Rath; 2006). This production method has several disadvantages: the intermediate has to be filtered due to the formation of gum-like byproducts, high energy need etc. In order to eliminate these disadvantages at the Department of Hydrocarbon and Coal Processing of University of Pannonia (thereafter Department) a new, radically initiated method was developed. The additives synthesized with this method had better performance compared to the commercial ones (Caprotti et al., 2007; Kocsis et al., 2003; Rang & Kann, 2003). During the research work the polyisobutylene of 800-1300 number average molecular weight was found to be the most advantageous for the production of such an additive structure, which is soluble in modern engine fuels due to its long hydrocarbon chain; and has such a polar functional group which is able to disperse the insoluble impurities (Beck et al., 2009a, 2009b, 2010; Bubálik et al., 2005; Kocsis et al., 2001).

One of the most important methods to measure the efficiency of detergent-dispersant additives is the engine test. Currently the Peugeot XUD-9 and the Peugeot DW-10 engine tests are the most common (Breakspear & Caprotti, 2007). The XUD-9 is a 1.9 litres indirect injection engine, while the Peugeot DW-10 is a 2.0 litres common rail diesel engine equipped with Siemens Euro 5 injectors (maximum injection pressure: 1600 bar). In 2008 March the CEC (Co-ordinating European Council for the development of performance tests for transportation fuels, lubricants and other fluids) accepted the F-98-08 injector test. According to it, the DW-10 engine is applied for the testing of diesel, biodiesel-diesel blends and deposit control additives. The DW-10 engine test does not substitute the XUD-9 engine test, because the latter is more suitable for measuring the efficiency of deposit control additives. The DW-10, however, is more sensitive for the efficiency of other additives, for example the metal deactivators.

2.2 Lubricity improver additives

The ultra low sulfur diesel – due to the strict hydrotreating - does not contain those compounds which provide good lubricity, and are originally present in the crude oil. In order to avoid wear, the application of synthetic lubricity improvers is necessary (Hancsók et al., 1999a, 2008a; Haycock & Thatcher, 2004; Kajdas & Majzer, 2003; Wei & Spikes, 1986). These additives are usually molecules with a long hydrocarbon chain and polar functional group. They form a layer on the metal surface by adsorption and decrease the friction coefficient.

Wear occurs in the fuel system, where different parts are moving on each other. As a consequence the most important thing is to form a protective layer on the surfaces by adsorption and/or chemisorption in order to reduce the metal-metal contact points (Figure 6 and 7) (Spikes & Wei, 1997; Wei & Spikes, 1986). The protective layer can be formed by the application of polar compounds.

Several compounds can be applied as lubricity improvers, such as different mixtures or esters of unsaturated hydrocarbon acids; alkenyl-succinimides; alcohols, acids, or esters having long hydrocarbon chain (Batt et al., 1996; Denecker, 2002; Hancsók et al., 1997; Haycock & Thatcher, 2004; Kajdas & Majzer, 1999; Spikes & Wei, 1997; Wei & Spikes).
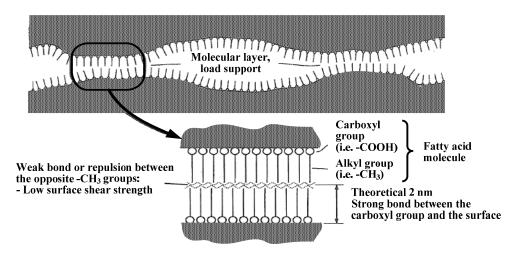

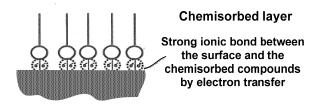Fig. 6. Mechanism of the formation of the film by adsorption

Fig. 7. Mechanism of the formation of the film by chemisorption

The latter mentioned esters can be produced from alcohols, vegetable oils or they can be bis-alkenyl-succinic esters, etc.

The most widely applied and standardized method for the measurement of the lubricity of diesel fuel is the HFRR test (High Frequency Reciprocating Rig, ISO 12156, ASTM D6079; VI. category): two metal test pieces are rubbed in continuous fuel flow and the friction and wear is measured. The wear of the upper test piece is measured in µm, according to the diesel standard (EN 590:2009) the wear has to be lower than 460 µm to assure enough lubrication - provided by the fuel – to protect the engine.

SLBOCLE (Scuffing Load Ball On Cylinder Lubricity Evaluator, ASTM D 6078; VI. category): two metal test pieces are rubbed in the presence of fuel, the test is carried out until the total wear of the test pieces, the load is measured.

Injector pump test (ISO/DIS 12156-1; III. category): wear on the test piece is measured in µm, and evaluated in the range of 1-10. The minimum requirement during the test is 6. The test load correlates to the load on the injector pump during 300,000 km normal operation. The test method has a high cost and is time consuming, therefore, it is not applied as a first selecting method, but only applied before the introduction of a new product. The results of the injector pump test correlates to the previously described two test results.

2.3 Corrosion inhibitors

Pure hydrocarbons of diesel fuel are not corrosive themselves. However, the sulfur or acidic compounds which can also be found in diesel fuel have a high corrosion effect on copper and its alloys. Storage conditions of fuel also have a significant effect on the corrosion properties of diesel fuel: during temperature change water can condensates on the roof or the wall of the storage tank and can enter into the fuel causing corrosion. These effects can be decreased by applying proper corrosion inhibitors. These additives, like the detergent-dispersants or the lubricity improvers, have polar functional group and long apolar hydrocarbon chain. They bond to the metal surface by chemisorption and form a protective layer. Corrosion inhibitors can be different alkyl- or polyalkyl-succinimides, their esters, dimer acids, amine salts (Hancsók et al., 1997; Haycock & Thatcher, 2004).

Among the different methods applied for measuring the performance of diesel fuel corrosion inhibitors, the copper strip corrosion and the steel drift tests are the most wide-spread. During the copper strip corrosion the cleaned and polished copper strips are kept in diesel fuel under controlled conditions (3h, 50°C) and after the test the colour change of the copper strips are evaluated visually according to the scale of the standard (EN ISO 216, ASTM 130). During the steel drift test water is added to the fuel to increase corrosion and after the controlled test (12h, 100°C) the corrosion degree of the steel drift is evaluated visually (ASTM 665). Both methods are based on increasing the corrosion properties of diesel fuel by elevated temperature and in case of the latter test also by the addition of water.

3. Development of multifunctional detergent-dispersant additives

In the recent years in the Department the aim of the research was to develop a multifunctional additive by applying the radically initiated synthesis method. The scope was to modify the structure of polyisobutylene succinimides in order to achieve other advantageous properties, but keeping their high detergent-dispersant efficiency (Russel,

1990; Hancsók et al., 1999b). Fatty acid methyl esters (biodiesel) have a reactive double bond, polar functional group and they have very good lubricity (Knothe, 2005a). Therefore, during our research the aim was to incorporate the fatty acid molecule into the succinimide structure.

One major issue of biodiesel blending into diesel fuel is the incompatibility of biodiesel with metals. Numerous publications report on corrosion of copper and its alloys due to contact with biodiesel, and as a result gum formation and acid number increase was also noticed. Due to the fact that long chain hydrocarbons having a polar functional group can form a protective layer on the metal surface, the corrosion inhibiting effect of the developed additive was also investigated. Another important effect of biodiesel on fossil fuels is that the fatty acid methyl esters enhance the biodegradability by co-metabolism (Pasqualino et al., 2006).

The reaction of polyisobutylene, maleic anhydride and fatty acid methyl ester was performed by radical initiation due to the fact that by the thermal reaction of maleic anhydride and fatty acid methyl ester gum-like byproducts formation was reported by other publications (Candy, 2005; Quesada, 2003).

3.1 Materials

Polyisobutylene succinimides are synthesised in two steps. In the first step commercial polyisobutylene (hereinafter: PIB) of 1000 number average molecular weight, fatty acid methyl ester (hereinafter: FAME), maleic anhydride (hereinafter: MA), a radical initiator and aromatic solvent was applied. The main properties of PIB and FAME are summarized in Table 1 and 2.

Properties	FAME
Mono-ester content, %	97.2
Density, g/cm^3	0.88
KV at 40 °C, mm^2/s	4.5
Flash point, °C	>110
Water content, %	0.02
Acid number, mg KOH/g	0.3
Methanol content, %	0.04
Iodine number, g/100g	112

Table 1. Main properties of the fatty acid methyl ester

Properties	PIB
Number average molecular weight	1050
Polydispersity, α	1.52
α-Olefin content, %	88
KV at 100°C, mm^2/s	192
Appearance	Transparent, bright
Flash Point (Cleveland), °C	204
Iodine number, g/100g	17

Table 2. Main properties of the polyisobutylene

For the second step of the synthesis the intermediate was diluted with base oil (SN-150) then the following amines were acylated: diethylene-triamine (hereinafter: DETA), triethylene-tertaamine (hereinafter: TETA), tetraethylene-pentaamine (hereinafter: TEPA), pentaethylene-hexaamine (hereinafter: PEHA), monoethanol-amine (hereinafter: MEA), diethanol-amine (hereinafter: DEA), piperazine, dibutyl-amine.

3.2 Methods

For the investigation of the properties of the intermediates and additives standard and in-house methods were applied, which are summarized in Table 3.

Properties	Methods
Kinematical viscosity	EN ISO 3104
Nitrogen content	Kjehldal method
Total Base Number (TBN)	ISO 3771
Total Acid Number	ISO 6618
Maleic-anhydride content	proprietary (titrimetic)
Active material content	local standard (column chromatography)
Molecular weight and distribution	GPC (PIB standards)
Washing Efficiency	proprietary (thin layer chromatography)
Detergent Index	proprietary (photometric)
Potential DD Efficiency (PDDE)	proprietary
Copper strip test	ISO 2160:2000
Steel drift test	ASTM D 665
Peugeot XUD9 engine test	CEC-PF-023
Lubricity improving effect (4ball test)	Modified ASTM D 2783-88
HFRR	ENISO12156

Table 3. Methods for measuring analytical properties and performance

3.2.1 Potential detergent-dispersant efficiency (thereafter PDDE)

According to our knowledge currently there is no standard method available for measuring the performance of the detergent additives of diesel fuels. Therefore, the potential detergent-dispersant efficiency (hereinafter: PDDE) method was applied, which was originally developed for motor oil additive testing.

The detergent-dispersant efficiency of the additives was measured by two methods: washing efficiency and detergent index.

The washing efficiency is measured by thin layer chromatography method. Its aim is to evaluate how effective the additive is for removing the impurities from the surface. For the test as the first step 1.5% additive is dissolved in SN-150 base oil. Then a suspension of 9.8 g of the mixture and 0.2 g carbon black is prepared by ultrasonic equipment. 10 µl of the suspension is placed on the chromatography paper and after letting it dry the paper is placed in a vertical position over heptane in such a way that only the lower ca. 0.5 cm of the paper is in contact with heptane. In this way the additive oil mixture – with the heptane - brings the suspension of carbon black upwards. The different additives bring the carbon black in different height of the paper based on the washing efficiency of the additive. The washing efficiency is measured in millimeters between the point where the suspension was put and the height where the oil brings the suspension with the heptane. Reproducibility of the measurement is ±5%.

The detergent index characterizes the dispersion stabilizing efficiency of the additive, thus, how they keep the impurities in a dispersed phase. The test is based on centrifugation and it is a modification of the original method developed at the Department. Additives with high dispersant efficiency do not let the suspended impurities accumulate even under centrifugation force. During the test the suspension prepared for the washing efficiency test is used. The suspension is diluted with petroleum in 1:5 ratio and centrifuged for 30 minutes at 500 1/min. After centrifugation the intensity of light through the upper part of the solution is measured at 530 nm. The detergent index is calculated from the intensity of light before and after the centrifugation according to the following:

$$DI=-(I_1/I_0)*100$$

Where DI: detergent index in %,
I_1: intensity of light in % transmitted through the blend containing carbon black,
I_0: intensity of light in % transmitted through the blend free of carbon black,
Reproducibility: ±1.
Based on the two methods potential detergent-dispersant efficiency of the additives is defined as follows:
$$PDDE=(DI+M)/225*100$$
Where DI: detergent index in %; its maximum value is 100%
M: washing efficiency in mm, maximum value is 125 mm
Reproducibility: ± 4%.

3.2.2 Measuring lubricity with four-ball machine
The lubricity improving effect of the additives was measured with Stanhope SETA four-ball machine. During the test the sample is put into a cup where 3 balls are in steady state and a fourth ball is pushed - with adjustable load - from above to the standing ones. The evaluation of the additive performance is carried out based on the wear scar diameter of the three standing balls and the friction coefficient. In order to improve the method a thermometer and a computer weres connected to the standard four-ball machine in order to register data and control the test. Figure 6 shows a simplified scheme of the apparatus. The lubricity of the diesel fuel additives is measured in 300 mg/kg concentration in diesel fuel under 300 N load during 1 hour. The average of the wear scar diameter of the three standing balls was evaluated (Bubalik et al., 2004, 2005).

3.3 Synthesis of additives having fatty acid methyl ester in their molecular structure
The production of the additives having fatty acid methyl ester in their molecular structure was performed in two steps. In the fist step intermediate was synthesized from PIB, MA, FAME, radical initiator and aromatic solvent in a four-neck flask equipped with a stirrer, thermometer, flow-back cooler and feeder (Hancsók et al., 2008b). The reactions were carried out at atmospheric pressure and at different temperatures (130-150°C) by applying different PIB:FAME:MA molar ratio, different solvent and initiator concentrate. The reactants were added in more portions, the reaction time was between 4 and 7 hours. The solvent and the unreacted maleic anhydrid were removed at 200°C under vacuum.
The intermediates were diluted with base oil in order to reduce their viscosity, then different amines were acylated by applying different amine:intermediate molar ratios. These reactions were carried out at 165-185°C, in 4-7 hours, by applying nitrogen atmosphere and slight vacuum. Unreacted amines and the formed water were removed at about 200°C under vacuum.
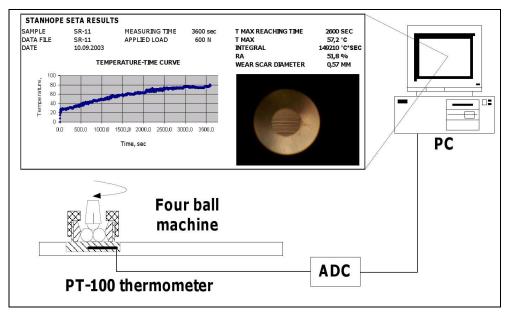
Fig. 6. Simplified scheme of the modified four-ball machine

The main properties of some intermediates are summarized in Table 4. Number average molecular weight of the PIB was about 1000, and that of the FAME about 300, while that of the intermediate was between 1300 and 1700. Based on these data we suppose that during the reaction the succinic structure is formed by one PIB, one MA and one or two FAME molecules.

Properties	KT-1	KT-2	KT-3	KT-4
Main parameters of the synthesis				
PIB:FAME:MSA molar ratio	1.0:1.1:1.0	1.0:1.1:1.1	1.0:1.1:1.3	1.0:1.1:1.4
Reaction temperature, °C	140	140	140	140
Properties of the intermediate				
Appearance	bright	Bright	Bright	Slightly opal
Active material content, %	64.5	63.3	69.3	64.2
Kinematical viscosity at 100°C, mm²/s	122.4	136.6	186.3	168.2
Acid number, mg KOH/g	62.3	67.9	70.6	84.5
MSA content, mg/g	0.9	2.3	1.2	1.3
Number average molecular weight	1300	1340	1500	1430

Table 4. Main properties of some intermediates

The additives showed in Table 5 were produced from the intermediate KT-3 by acylating different amines. All additives synthesised by applying polyethylene polyamines had high detergent-dispersant efficiency and high total base number (hereinafter: TBN). The other amines resulted in additives with lower PDDE and TBN, except for piperazine, which had high detergent-dispersant efficiency and at the same time low total base number (see Table 5 and Figure 7). The low total base number improves the compatibility of the additive with

fluoroelastomers, while the high total base number increases the acid neutralising property of the additive. The polyethylene polyamines and piperazine let us produce additives with high detergent-dispersant efficiency and an appropriate total base number, depending on what the application field requires.

Properties	FP-1	FP-2	FP-3	FP-4	FP-5	FP-6	FP-7	FP-8
Acylating agent	TEPA	DETA	PEHA	TETA	MEA	DEA	Pipe-razine	Dibutyl-amine
Average molecular weight of the amine, g/mol	189	103	232	146				
Molar ratio	1,0:1,0	1,0:1,0	1,0:1,0	1,0:1,0	1,0:1,0	1,0:1,0	1,0:1,0	1,0:1,0
Appearance	Bright	Bright	Bright	Bright	Bright	Bright	Bright	Bright
TBN, mg KOH/g	54.9	29.0	60.5	43.7	2.1	6.5	7.0	2.4
Nitrogen content, %	2.5	1.58	2.43	1.98	0.21	0.56	0.6	0.38
Average molecular weight	1500	1750	1350	1725	1350	1450	2350	5400
3 % (based on active material content) additive in SN 150 base oil								
V.I.E	112	108	107	106	105	106	107	106
Detergent Index, % (max. 100)	100	100	100	100	0	100	100	43
Washing Efficiency, mm (max. 125)	94	96	99	93	13	62	95	11
Potential Detergent-Dispersant Efficiency, % (max. 100)	86	87	88	85	6	72	87	24

Table 5. Main parameters of the additives having FAME in their molecular structure
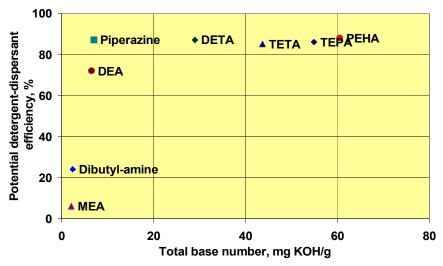

Fig. 7. PDDE of the additives in function of their TBN

The additives synthesized with polyethylene polyamines had such a strong apolar functional group that they were able to form a protective layer on the metal surface, meanwhile their long apolar hydrocarbon chain provided excellent solubility in hydrocarbons. Therefore, their corrosion inhibiting effect was investigated by applying two test methods: copper strip corrosion and steel drift test. The tests were performed in diesel fuel without biodiesel and diesel fuel with 7% biodiesel content. The additive concentration was 20 mg/kg in all cases (Table 6). Copper strip corrosion classification of the diesel fuel without additive was 1B, with the additives it became 1A. During the steel drift test after 6 hours the corrosion degree of the base diesel fuel was quite high, after 12 hours it was over the limits of the measurement. The additives decreased the corrosion during the 12 hours test; however they could not inhibit it completely.

The diesel fuel having 7% biodiesel had disadvantageous corrosion properties both during the copper strip and the steel drift test. Based on the results it was established that all tested additives decreased the corrosion degree of the 7% biodiesel containing diesel fuel. The corrosion inhibiting effect of the additives can be explained by the presence of both polar and apolar function groups in the molecular structure. The polar group enables the additives to bond to the metal surface by chemisorption, while the apolar functional group enables the solubility in hydrocarbons.

	Addtive applied in 20 mg/kg	Copper strip test, classification	Steel drift test, classification 6h	Steel drift test, classification 12h
Diesel fuel	-	1B	3	n/a
	S-1	1A	0	1
	S-2	1A	0	1
	S-3	1A	0	1
	S-4	1A	0	1
B7 (7% biodiesel in diesel fuel)	-	3A	3	n/a
	S-1	1A	0	1
	S-2	1A	0	1
	S-3	1A	0	1
	S-4	1A	0	1

Table 6. Corrosion inhibiting effect of the additives

3.3.1 Molecular structure of the additives having fatty acid methyl ester in their molecular structure

For determining the molecular structure GPC, IR and NMR spectroscopy tests were carried out.

The number average molecular weight of intermediates was in the range of 1400-1700 and the polydispersity was in the range of 1.66-1.84. It suggests that the polyisobutylene and also one or two fatty acid methyl ester compounds linked into the molecular structure. The highly reactive allyl and bis-allyl position carbon atoms (Knothe, 2005b) of the fatty acid

methyl ester can react with maleic anhydride to form a succinic anhydride molecule. The results published by Candy (Candy et al., 2005) approved that there is an ene-reaction between succinic anhydride and fatty acid methyl ester.

On the basis of IR spectroscopy data (Hancsók et al., 2006, 2008) and the ^{13}C and ^{1}H NMR tests it was concluded that during the reaction of polyisobutylene, maleic anhydride and fatty acid methyl ester two alkyl chains can substitute a maleic anhydride. Based on the GPC, IR and NMR tests (see Figure 8), the most possible structure is that a polyisobutylene and a fatty acid methyl ester molecule are substituted a maleic anhydride as shown in Figure 9.

3.4 Synthesis of additives having fatty acid methyl ester and styrene comonomer in their molecular structure

The additives having fatty acid methyl ester in their structure were produced in two steps, as mentioned in the chapter before. In order to incorporate the styrene comonomer to the additive, further reaction steps were necessary. Polyisobutylene, maleic anhydrid and styrene were reacted in the presence of a radical initiator and aromatic solvent at the same reaction parameters that were applied for the production of the intermediate with FAME in
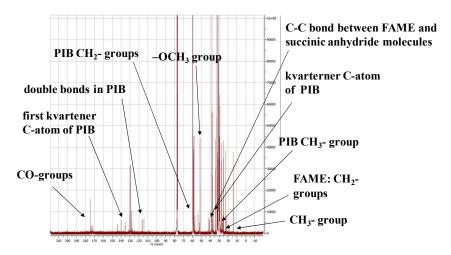

Fig. 8. 13C NMR spectra of the intermediate

Fig. 9. The most possible structure of the intermediate

its structure. The intermediate containing the styrene was diluted with base oil, and then reacted with the previous additives (FP). In such a way a bis-succinic structure was obtained (see Figure 4).

The quality of the additive highly depends on the process parameters of the synthesis. The main properties of some intermediates (synthesized with styrene, without FAME) are summarized in table 7. The reactions were performed at the same temperature, but with different feedstock molar ratio, as a result the properties of the intermediates were significantly different. Intermediate TS-2 was found to be the most advantageous with its higher active material content, acid number and number average molecular weight. It was found that the increase of MA ratio in the feedstock composition leads to significant change in the acid number of the intermediate.

Properties	TS-1	TS-2	TS-3	TS-4
PIB:MA:styrene molar ratio	1.0:1.9:1.1	1.0:2.0:1.2	1.0:1.8:1.1	1.0:1.9:1.2
Reaction temperature, °C	140	140	140	140
Properties of the intermediate product				
Appearance	bright	bright	bright	cloudy
Active material content, %	55.8	72.3	59.6	63
Kinematical viscosity at 100°C, mm²/s	94.0	141.2	195.8	163.4
Acid number, mg KOH/g	145	158	152	149
MA content, mg/g	1.3	1.5	1.2	1.2
(number average molecular weight)	1570	1950	1860	1700

Table 7. Main properties of some intermediates with styrene

The intermediates having styrene comonomer were reacted with the additives FP-1 and FP-3 which have fatty acid methyl ester in their structure. The result of the reaction was a bis-succinic type additive (see Figure 4) with relatively high detergent-dispersant efficiency, but with a relatively lower base number compared to the reference commercial mono-bis-succinic type additive.

The total base number of the FPS-1 – FPS-4 additives was significantly lower than that of the FP-1 and FP-3 additives (~30-60 mg KOH/g) synthesized with polyethylene polyamines, while their detergent-dispersant efficiency was quite similar.

The viscosity index improving effect of all the additives was tested in 1.5% active material concentration in SN-150 base oil. The styrene containing additives had a significant viscosity index improving effect, as a result their application as engine oil additives can be considered in the future.

The lubricity of the FAME (S-1 – S-4); and the FAME and styrene containing additives (PSS-1 – PSS-4) was tested in 300 mg/kg concentration in diesel fuel by the four-ball machine. During the four-ball test the applied load was 300 N for 1 hour. The average wear scar diameter measured on the three standing balls and the results of the HFRR test are summarized in Figure 10. Among the additives synthesized with FAME (without styrene) FP-1 was found to have the best performance. The additives synthesized with both FAME and styrene resulted to be the most advantageous in increasing the lubricity of the base diesel fuel (GO). FPS-2 and FPS-4 additives had the best performance, these additives were synthesized with high styrene:maleic anhydride molar ratio. FPS-2 was produced from the FP-1 additive which was acylated with TEPA, while FPS-4 was produced from FP-3 additive which was acylated with PEHA. Both TEPA and PEHA are long chained amines among the tested ones, with a high total base umber.

Properties	FPS-1	FPS -2	FPS -3	FPS -4	Reference
Intermediate	TS-1	TS-2	TS-1	TS-2	-
Acylating agent	FP-1	FP-1	FP-3	FP-3	-
Molar ratio of intermediate and acylating agent	1.0:1.0	1.0:1.0	1.0:1.0	1.0:1.0	-
Appearance	Bright	Cloudy	Bright	Bright	Bright
TBN, mg KOH/g	11.8	10.3	12.6	13.5	40
Nitrogen content, %	1.98	1.58	2.43	2.50	3,22
1,5 % (based on active material content) additive in SN 150 base oil					
V.I.E	108	110	124	119	104
Detergent Index, % (max. 100)	100	100	100	100	100
Washing Efficiency, mm (max. 125)	92	95	94	92	90
Potential Detergent-Dispersant Efficiency, % (max. 100)	85	87	86	85	85

Table 8. Succinic additives containing FAME and styrene comonomer

The lubricity improving effect of the additives was also tested with HFRR machine. The results showed the same tendency among the efficiency of the additives as in case of the four-ball test.
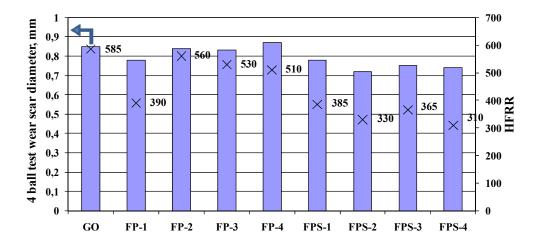

Fig. 10. Lubricity improving effect of the additives in 300 mg/kg concentration in base diesel fuel (GO)

4. Summary

By incorporating fatty acid methyl ester to the structure of the polyisobutylene succinimide a new additive was developed which had high detergent-dispersant efficiency and an additional lubricity improving and corrosion inhibiting effect.

The lubricity improving effect of the abovementioned additives could be further increased by incorporating not only fatty acid methyl ester, but also styrene comonomer to the additive. The detergent-dispersant efficiency of the additives remained relatively high, while their viscosity improving effect increased significantly. Their relatively low total base number ensures good compatibility with fluoroelastomers, thus in the near future the application of these additives in engine oil compositions can be promising research field.

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6. References

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Biodiesel- Quality, Emissions and By-Products

Edited by Dr. Gisela Montero

This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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