Imidazoline Type Dispersants for Fuels

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Two carboxylic dispersant with imidazoline structure were synthesized and tested in order to improve the performance of the engine by reducing deposits on fuel circuit. Characterization of dispersants was made by determination of amino nitrogen. The dispersant characteristics were evaluated by measuring the stability of the suspension and the sedimentation rate of the nano-sized metal powders of iron and copper with a Turbiscan Lab. The stability of the suspension increase with amino nitrogen content of the dispersants with similar structure. The increase in additive content of 0 to 100 ppm improves the suspension stability. Carboxylic compounds with imidazoline structure can be used as diesel fuel dispersants, dispersant properties being more pronounced with the higher amino nitrogen content.

Keywoords: dispersant, suspension stability, fuel, imidazoline

Modern automotive fuels contain additives to improve performance in all engines, preferably "environmentally friendly". Dispersants are used to prevent sedimentation deposition, precipitation, agglomeration, flocculation, coagulation [1] that can lead to the formation of deposits in the fuel system and combustion chamber so that their presence in gasoline and /or diesel have an important role in improving the operation of motor vehicles. Thus the Directive 2009/30/EC of the European Parliament recommends the introduction of detergents to clean the engine and thus contribute to reducing greenhouse gas emissions.

Many types of these compounds have been proposed, tested and utilized. Detergent properties of gasoline conferred and structures obtained by Mannich synthesis of alkylene bis succinimides, nonylphenol (now banned in the EU) and paraformaldehyde [2].

The Chevron-Texaco Company recommended a mixture of ethylenediamine carbamate and adducts of dodecylphenol with butylene oxide to improve detergent properties of fuels [3], although it is known that non-ionic surfactants (detergents of additives) type adducts of alkylene oxides are thermally unstable, are self oxidizes from 100^{0}C, releasing heat [4].

The Mobil Oil Company claims a detergent-dispersant additives for fuels and lubricants obtained by grafting a mono-ester (aromatic dicarboxylic acid with monohydroxy polyalkylene-ether) with a polyalkylene polyamine succinimides [5,6].

Ester functional group in the succinimide structure gives detergent-dispersant properties for fuels especially in the area of valve [7]. End products with molecular weights in the range 700-2500 are stable at a temperature up to 200^{0}C.

Besides dispersed actions these compounds may have other functions such as detergent [8-10], corrosion inhibitors [11, 12], antioxidant [13, 14] and others. Multi-functionality of the additive allows to be obtained more benefits with just one product. Zavarukhina, and others have investigated the effect of Cetane-boosting, antiwear, depressant, dispersing, and multifunctional additives on the quality indexes of summer-grade diesel fuel. The highly effective multifunctional Evropris additive simultaneously improves Evropris five indexes. This allowed for the obtention of fuel based on S-grade DF (GOST 305-82) that satisfies the requirements of European Standard EN 590 [15].

Literature suggests the term of hyperdispersant for a category of dispersants polymers designed to be effective in stabilizing dispersions of solids particles in organic liquid media. Thus ZHANG Bao-Hua and others have synthesized hyperdispersants of 12-hydroxy-stearic acid, stearic acid with polyethyleneimines, which are used to improve the dispersion properties of the nano-TiO_2 in the resin solution at low concentration. They also studied the influence of hyper-dispersant on the system viscosity and stability [16].

Besides controlling of soot depositing [17], dispersants act on other fine particles that are found in the fuel (such as metallic iron and copper), because the fuel comes in contact with the metal parts of the combustion system [18].

The research carried out aimed the preparation and testing of two carboxylic dispersant with imidazoline structure, to improve the functioning of engine by reducing deposits in the fuel system. Imidazolinium derivatives which are of interest include the product characterized by the presence of long hydrocarbon chains (linear or branched with 8-24 carbon atoms) grafted on the imidazoline core, and by the possible presence of a polyalkylene-polyamine chain linked to one of the tertiary nitrogen atoms from the heterocyclic ring.

Experimental part

Synthesis of 1,2-disubstituted alkyl imidazolines was performed in a three-necked glass flask equipped with downward condenser and mechanical stirring. The stirring rate was maintained at 700 rot/min for each experiment.

The raw materials used in the preparation of dispersants were behenic acid 99% (Aldrich), triethylentetraamine (technical degrees, 60% Aldrich) and higher polyamine blend, Berolamina 20 (AkzoNobel) whose characteristics are shown in table 1. The experimental program of the etherification was performed for 6 h at 230°C. The behenic acid/polyamine masic ratio was 2.12/1 for first dispersant

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Table 1
CHARACTERISTICS OF BEROLAMINA 20

Boiling point, ^{0}C (760mmHg)	> 270
Flash point, ^{0}C (Pensky-Martens)	180 ^{0}C
Vapor pressure, kPa (20 ^{0}C)	0.002
Density, kg/m^3 (20 ^{0}C)	1070
Viscozity, mPa*s (20 ^{0}C)	40

Table 2
CHARACTERISTICS OF IRON AND COPPER PARTICLES

Characteristics	iron	copper
Aspect	gray powder	orange-brown powder
Density	7,86 g/cm^3	8.92 g/cm^3

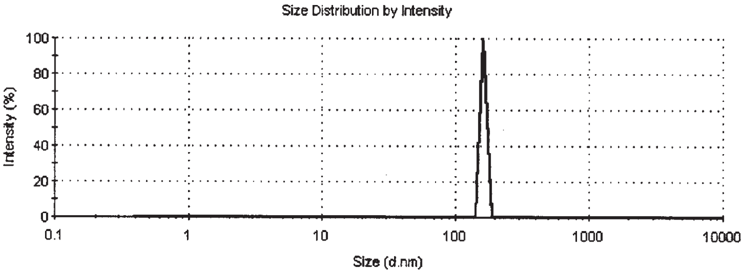

Fig. 1. Distribution of iron particle size by DLS

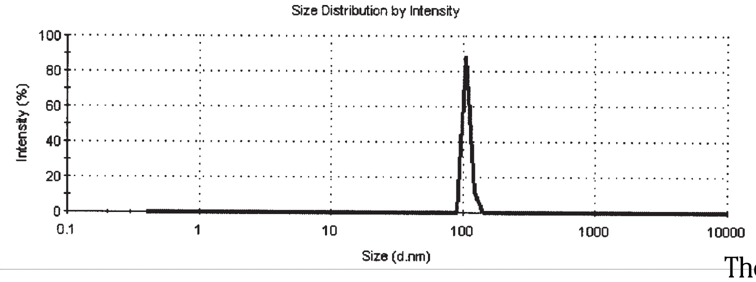

Fig. 2. Distribution of copper particle size by DLS

Table 3
TECHNICAL SPECIFICATIONS OF DIESEL

Cetane number, min	51
Cetane index, min	46
Density at 15°C, kg/m^3	820-845
Polycyclic aromatic hydrocarbons, %(m/m), max	11
Sulfur content, mg/kg, max	10,0
Ash content, %(m/m), max	0.01
Water content, mg/kg, max	200
Stability to oxidation, g/ m^3 , h	25
Viscozity at 40 °C, m^2/s	2,00-4,50

(noted BT dispersant) and for second dispersant (noted BB dispersant) the behenic acid / Berolamina 20 was 1.03/ 1. Characterization of dispersants obtained was performed by determining the content of amino nitrogen using a Mettler Toledo DL 28 titrator.

The effectiveness of dispersants prepared was evaluated by studying the stability over time of the suspension of particles in diesel. The particles used in the study are metal powders of Fe and Cu. The distribution of particle sizes of iron and copper was measured with a particle size measurement by dynamic light scattering (DLS). The instrument used for measuring is a Nano ZS (Red badge) and the particle size field is 0.6 nm - 6 microns, their distribution being uni-nodal (fig. 1). Table 2 shows the characteristics of metal particles. This was added in gas oil with or without additives in a proportion of 0.5%, 0.8% and 1.3% weight. The BB and BT dispersants content in the gas oil was 100 ppm, 60 ppm and 30 ppm.

The specifications of gas oil used are presented in table 3. Dispersants characteristics were evaluated by measuring the stability of the suspension and the sedimentation of the particles with a Turbiscan Lab. Change detection was evaluated both in transmission and backscatter depending on the moving of particles (aggregation and sedimentation). Data were collected every 150 s for 30 min, in total 12 scans for each sample. It was verified that the samples did not adhere to the walls of the tube.

Results and discussions

Figures 3 and 4 show the titration curves to determine of the amino nitrogen content of the two dispersants BB and BT.

The amine nitrogen content of the two dispersants are presented in table 4.

Table 4
NITROGEN CONTENT OF THE AMINE DISPERSANTS

No. crt.	Dispersant type	Amine nitrogen content, %
1.	BT dispersant	8.47
2.	BB dispersant	1.43

Figures 5, 6 and 7 show the stability of the suspension and a sedimentation speed of the copper particles determined by a Turbiscan Lab. The sedimentation of the suspension was revealed in backscattering profiles.

For the metal particles present in diesel without additives (fig. 5), the backscattering profiles as a function of tube height (0–50 mm) are changing rapidly because the aggregation occurs in the middle of the cell, followed by sedimentation on the bottom of the cell. Dispersion stability was improved by adding of the BT and BB dispersant (fig. 6 and fig. 7). Sedimentation of the particles in the bottom of both formulations was lower compared to diesel without additives.

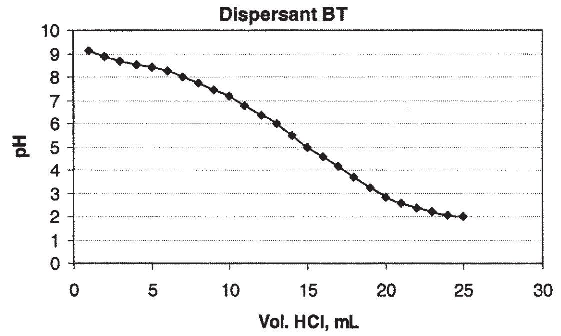

Fig. 3. Titration curve for dispersant BT (HCl solution, 0.1 N; f=0.9988)

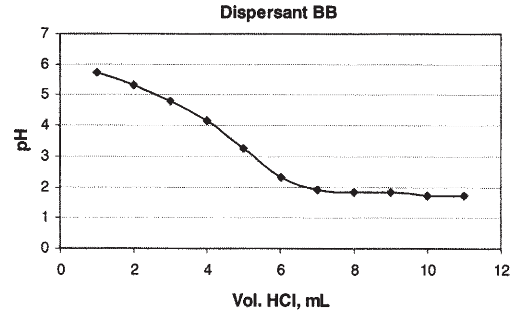

Fig. 4. Titration curve for dispersant BB (HCl solution, f=0.9988)

Figure 8 shows computed peak thickness kinetics as a function of time in the clarification regime of the cell. The migration rates of the Cu microparticles were computed from the slope of the curves. Non-dispersed Cu microparticles had a migration rate of 0.34 mm/min, while BT dispersant had a migration rate of 0.06 mm/min and BB dispersant had a migration rate of 0.13 mm/min. We were able to quantify the dispersion stability by the delta backscattering profiles and the peak thickness as a function of time. We found that the suspension of diesel containing microparticles of Cu in the presence of dispersant BT was more stable than with BB dispersant. Thus BT dispersant improved suspension stability more than dispersant BB. Moreover the performance of the dispersant increases with the amine nitrogen content of the dispersant for the dispersants of similar structure.

The increase in additive content of 0 to 100 ppm improves the stability of the suspension, as pointed out the reduction of the change in backscattering (fig. 9). Increased content of dispersed particles lowers the stability of the suspension.

Figures 10 and 11 represent the variation curves for delta backscattering with time, for diesel fuel without additives and with 30 ppm, 60 ppm and 100 ppm of BT dispersant, which contains 0.2 g Cu and 0.2 g Fe.

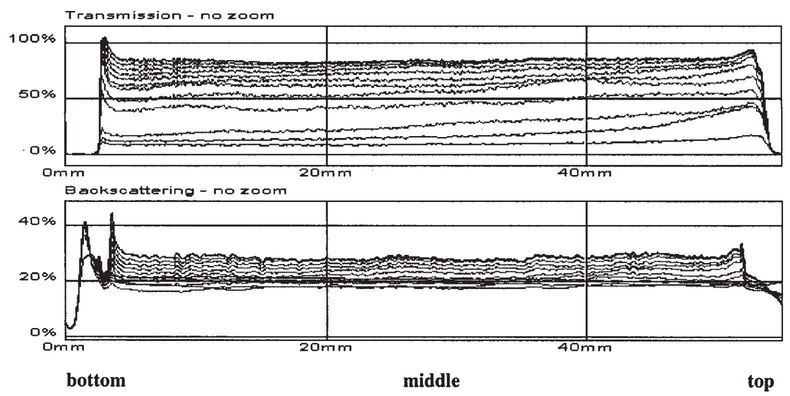

Fig 5. Transmission (T) and backscattering (BS) data (%) for metal micropowdered suspensions of copper in diesel without additives (data are given for different periods of time - arrows from top to bottom, 0–30 min)

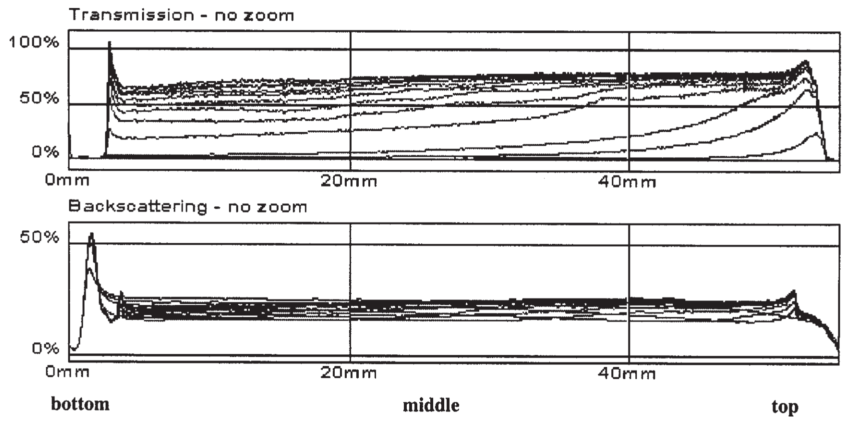

Fig 6. Transmission (T) and backscattering (BS) data (%) for metal micropowdered suspensions of copper in diesel fillers with BT dispersant; (data are given for different periods of time - arrows from top to bottom, 0–30 min).

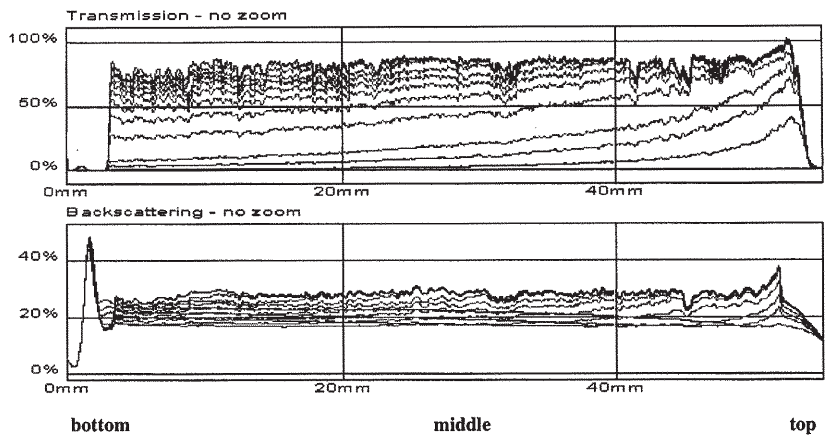

Fig 7. Transmission (T) and backscattering (BS) data (%) for metal micropowdered suspensions of copper in diesel fillers with BB dispersant (data are given for different periods of time - arrows from top to bottom, 0–30 min).

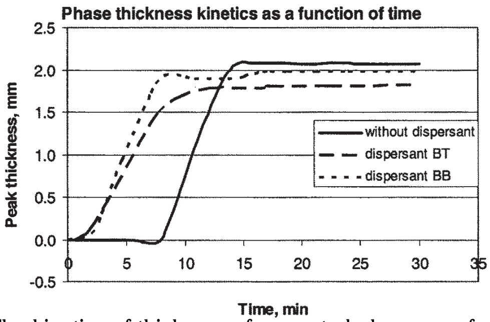

Fig. 8. The kinetics of thickness of separated phase as a function of time in the absence of dispersants and in the presence of dispersants BT and BB

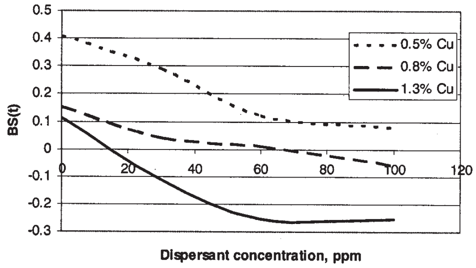

Fig. 9. Variation of backscattering with BT dispersant concentration for different content of copper particles

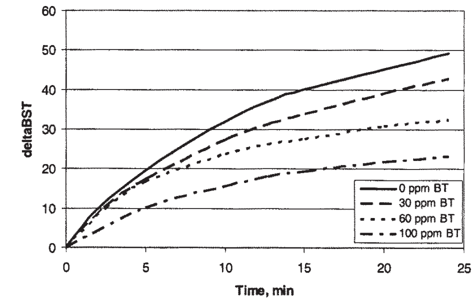

Fig. 10. Delta backscattering variation for diesel fuel without additives and with 30 ppm, 60 ppm and 100 ppm of BT dispersant, which contains 0.5% Cu

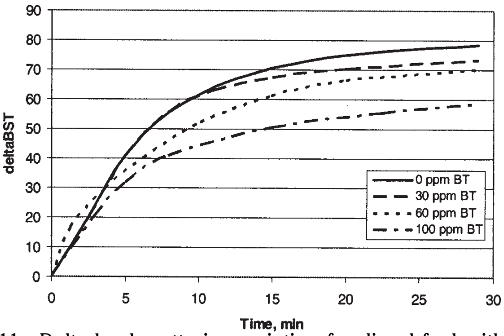

Fig. 11. Delta backscattering variation for diesel fuel without additives and with 30 ppm, 60 ppm and 100 ppm of BT dispersant, which contains 0.5% Fe

The diesel fuel which contains 100 ppm of BT dispersant has the best kinetic stability, both when using copper and iron particles. Note that kinetic stability is better when using copper nanoparticles than in those of iron nanoparticles.

Conclusions

The purpose of the research was was to prepare and test two carboxylic dispersant with imidazoline structure, for improving engine functioning by reducing deposits on fuel circuit.

The effectiveness of the dispersants prepared was evaluated by studying the stability of the suspension of Fe and Cu metallic particles in diesel fuel.

The distribution of particle sizes of iron and copper was measured by dynamic light scattering.

Dispersant characteristics were evaluated by measuring the stability of the suspension and the sedimentation rate of the particles with a Turbiscan Lab.

Dispersion stability was improved by adding dispersants with imidazoline structure.

Dispersant performance increases with the amino nitrogen content of the dispersant, for the dispersant with similar structure.

The increase in additive content from 0 to 100 ppm improves the suspension stability.

Diesel fuel with 100 ppm BT dispersant shows a better kinetic stability both for the Cu and for the Fe nanoparticles. The kinetic stability is better for Cu nanoparticles than for Fe nanoparticles.

Carboxylic compounds synthesized with imidazoline structure can be used as diesel fuel dispersants, dispersant properties being more pronounced with the higher amino nitrogen content.

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