STUDY OF MODIFIED OXYETHYLATED NONYLPHENOL FORMALDEHYDE OLIGOMERS AS ANTIOXIDANTS AND DEPRESSOR ADDITIVES TO DIESEL FUELS

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Abstract: *It's known that hydropurification process of diesel fuels leads to elimination of sulfur-, nitrogen- and oxygen-containing compounds in their composition and causes in a violation of chemical stability, compensated by the use of additives. Heteroatom-containing phenol and alkylphenol-formaldehyde oligomers are widely studied as effective multifunctional additives for fuels and oils. Imidazolinamine-modified oxyethylated nonylphenol-formaldehyde oligomers were studied as multifunctional diesel fuel additives. It was established that addition of imidazolinamine-modified oxyethylated nonylphenol-formaldehyde oligomers to hydropurified diesel fuel causes a decrease in the amount of sediment formed from 2.5 to 0.2 mg/100 ml of product; freezing point also decreases from -10 to -18℃. It was proved that the use of synthesized additives in hydropurified diesel fuel improves some of its performance properties.*

Keywords: *oxyethylated nonylphenolformaldehyde oligomers, imidazolinamines, modification, thermal-oxidative stability, depressor properties, diesel fuel, additives.*

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1. Introduction

New additives were developed and obtained as a result of the improvement and development of technology and stricter environmental standards [1, 2]. Currently, it's a trend to produce engines operating at higher temperatures leading to intensive use of antioxidant additives. Heteroatom-containing phenol and alkylphenol-formaldehyde oligomers are widely studied as effective antioxidant additives for fuels and oils. Industrial additives such as CIATIM-339, AKI-101, Borin, BFK are known as increasing thermal-oxidative stability, as well as detergent and depressant additives for motor oils [3-5], some of them are used as anti-corrosion and anti-wear additives [6-8].

Many Azerbaijani researchers have carried out the studies in the direction of the synthesis and use of phenol and alkylphenol-formaldehyde oligomers modified with nitrogen and sulfur-containing compounds, their calcium salts, as well as other products of their transformations relate specifically to their use as additives for various purposes, in particular improving thermal-oxidative and anti-corrosion stability [9-11].

Thermal-oxidative stability of motor oil was improved by phenol oxypropylation in the presence of benzguanoamine and adding the resulting product in an amount of 1% to M-8 motor oil. The sediment amount was 0.5%. It's explained by the presence in the macromolecules of oligomers of fragments suppressing the formation of radicals formed during the oxidation process. These fragments, along with the mobile hydrogen atoms of phenol, also include the lone electron pair of nitrogen atoms of amine fragments. Viscosity indicators also increased up to 15.4% [12]. Influence of phenolic and functional nitrogen groups on the growth of microorganisms was considered [13].

It is known that hydropurification process of diesel fuel leads to elimination of sulfur-, nitrogen- and oxygen-containing compounds in its composition that in turn leads to a violation of its chemical stability during storage for a certain time. A darkening is observed in the color of the fuel, and the amount of sediment increases as a result of a decrease in thermal-oxidative stability. It should be noted that, depending on the composition of the diesel fuel, the ignition cycle delay time in diesel engines is different and characterized by cetane number of the fuel. It is known that in summer the use of diesel fuels with a cetane number of 40-45 is the norm, but for winter diesel fuels the cetane number should not be lower than 45. An increase in the cetane number of diesel fuels also leads to a decrease in the emission of NO_x and CO gases into the atmosphere, which in turn reduces environmental tension. As the temperature decreases, the viscosity of all diesel fuels also decreases. Diesel fuels contain large quantities of hydrocarbons with a high melting point. The most important of them are alkanes of normal structure. As a result of a decrease in temperature, hydrocarbons with a high melting point form a precipitate in the form of crystals of various structures, the fuel becomes cloudy and there is a danger of clogging the injectors with paraffin crystals. Therefore, the cloud point of diesel fuels should be several degrees lower than the temperature of its use. As the temperature decreases, hydrocarbons with high melting points in cloudy fuel combine into large crystals and form a spatial network in the pores of which liquid hydrocarbons are retained. Thus, at a certain temperature, the fuel loses its fluidity. This temperature is taken as the freezing point of the fuel.

Considering the aforementioned, *the purpose of this study* was to examine the use of oxyethylated nonylphenol formaldehyde oligomers (ONFFO) modified by imidazolylamine as antioxidant additives in diesel fuel.

2. Experimental Part

Imidazolinamines were synthesized based on natural petroleum acids (NPA) and polyethylenepolyamines (PEPA) by a well-known method [14] and used in the modification process of oxyethylated nonylphenol-formaldehyde oligomers. The ratio of acids to polyamines was 1-2-3:1. Modification process of ONPFO with imidazolinamines was carried out at 95-98°C. Appearance of turbidities in the reaction mixture, indicating the formation of condensation centers and formation of an oligomeric chain caused a decrease in the temperature to 50°C, at which the required amount of modifier was introduced into the system in parts and the temperature again was raised to 95-98°C. At this temperature, the reaction continued for the required amount of time until the formation of resin.

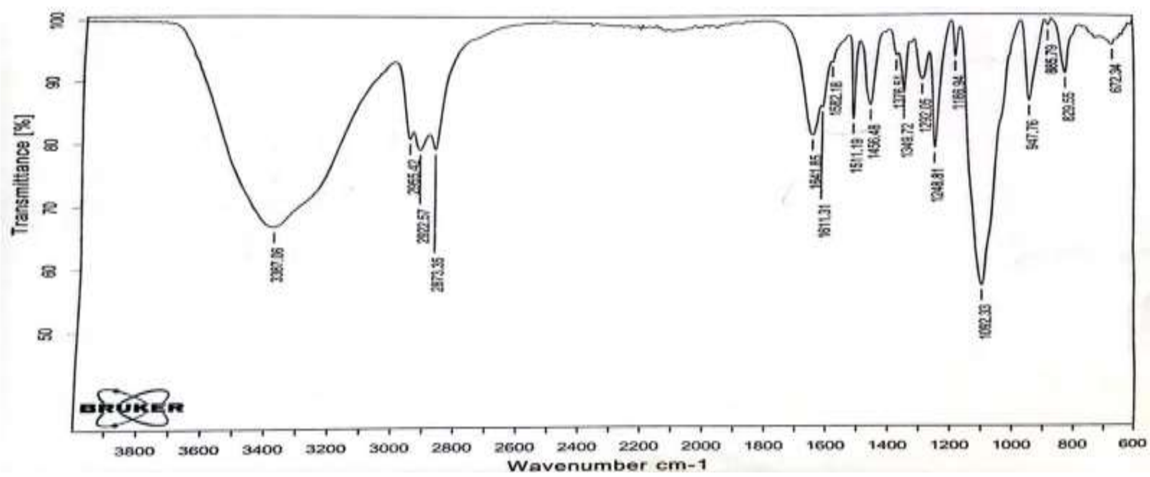

Fig. 1. IR spectrum of ONPFO modified with imidazolinamine (NPA:PEPA = 1:1)

The spectra of ONPFO modified with imidazolines were recorded on LUMOS IR-Fourier spectrometer from BRUKER (Germany) in the wave frequency range 600-4000 cm^{-1} and are presented in Fig. 1, 2, and 3.

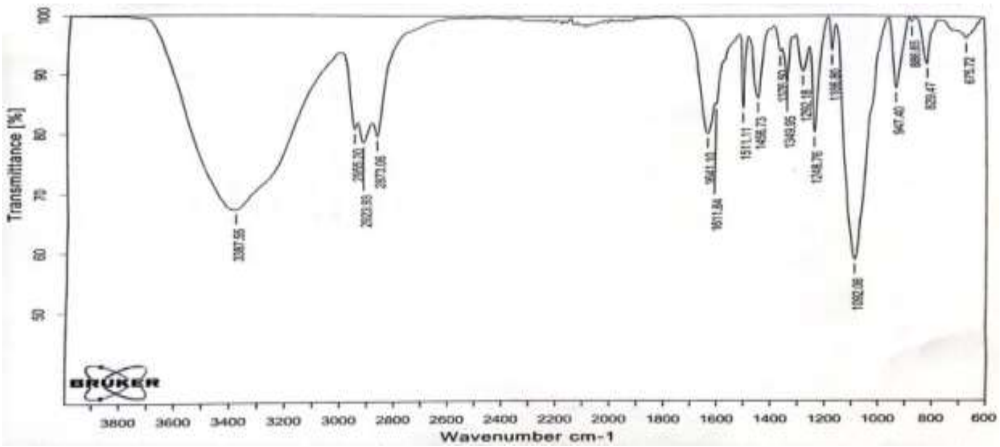

Fig. 2. IR spectrum of ONPFO modified with.imidazolinamine (NPA:PEPA = 2:1)

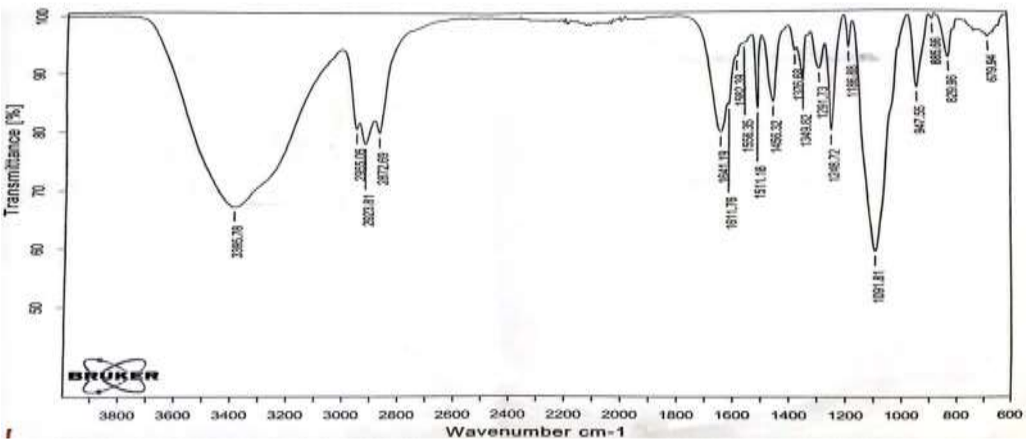

Fig. 3. IR spectrum of ONPFO modified with.imidazolinamine (NPA:PEPA = 3:1)

For the purpose of studying the thermal stability of ONPFO modified with imidazolinamines based on NPA and PEPA, thermogravimetric (TGA) and differential thermal (DTA) analyzes were carried out. Determination of thermal stability were carried out on (TG/DTG/TG/DTA) thermal analyzer "YUPİTER STA 449 F3" from the German company NETZSCH in an inert nitrogen medium (oxidation processes are excluded) in the temperature range 20-650°C with a heating rate of 10K/min. Thermal stability of ONPFO, TGA and DTA curves of oligomers are presented in Fig. 4, 5, and 6.

3. Results and Discussion

IR spectra of imidazolinamine-modified different compositions of ONPFO are also identical with slight shifts. Consider the example of ONPFO modified with imidazolinamine in a molar ratio of 3:1 (Fig. 3). The spectrum showed: deformation vibrations at 1376, 1456 cm^{-1} and valence vibrations at 2872, 2923, 2955 cm^{-1} of C-H bond of CH_2 groups; deformation 1556 cm^{-1} vibrations of N-H bond; valence vibrations at 1186 cm^{-1} of C-N bond; valence vibrations of C=N bond at 1641 cm^{-1}; deformation vibrations of C-H bond of benzene ring at 829 cm^{-1}; valence vibrations at 1611 cm^{-1} of C-C bond of benzene ring; valence vibrations of O-H bonds at 3395 cm^{-1}; valence vibrations of C-O-C ether bonds at 1248 cm^{-1}.

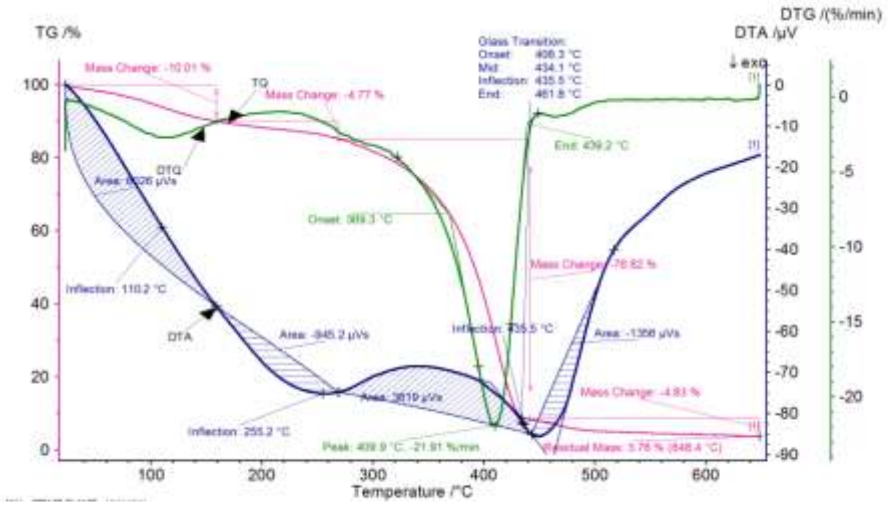

Fig. 4. TGA and DTA curves of ONPFO modified with imidazolinamine (NPA:PEPA = 1:1)

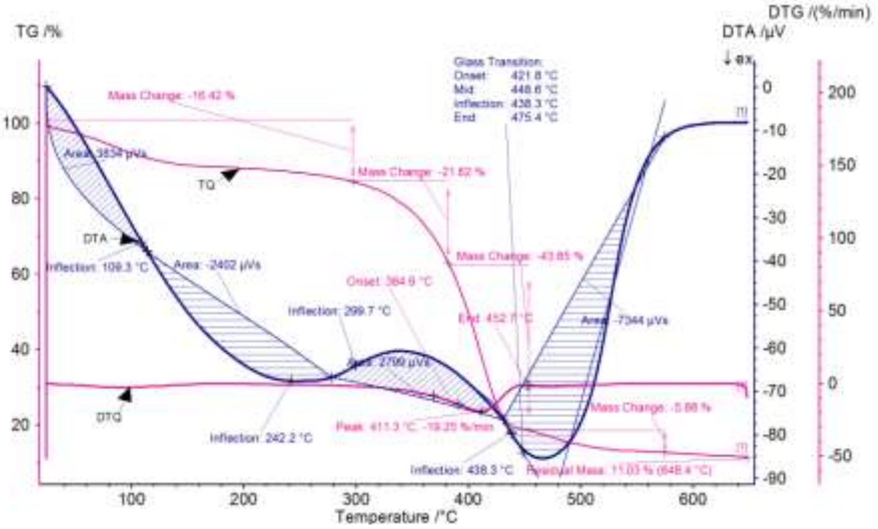

Fig. 5. TGA and DTA curves of ONPFO modified with imidazolinamine (NPA:PEPA =2:1)

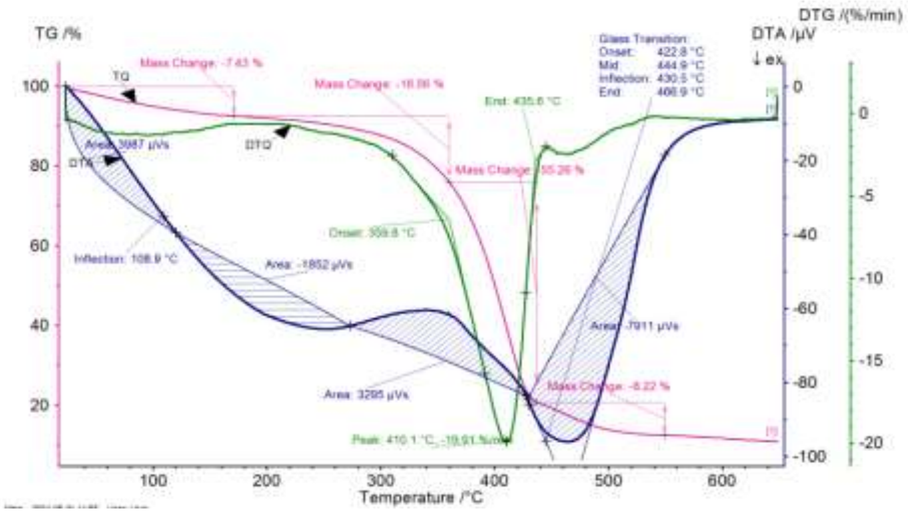

Fig. 6. TGA and DTA curves of ONPFO modified with.imidazolinamine (NPA:PEPA =3:1)

According to the analysis of IR spectra, a mechanism was proposed for modification process of ONPFO with imidazolinamines of various compositions.

As is evident from TGA curves of the studied samples, destruction occurs in several stages. In the TGA curve shown in Figure 4, the mass loss up to 200°C is 10%, from 200 to 300 °C – 4.77%. In the temperature range from 300 to 440 °C, deep destruction occurs, which ends at 462 °C, the peak of destruction occurs at 435°C. Above the specified temperature, residual destruction occurs, weight loss is 4.83%. At a temperature of 650 0C, the residual mass is 3.76%. The first inflection of DTA curve occurs at 160°C. Up to the specified temperature, destruction is accompanied by a large area of endo-effects - 8026 μVs. The second inflection is observed at a temperature of 255°C and is accompanied by exo-effects with a small area of 945 μVs. The third inflection is observed at a temperature of 435.5°C and is accompanied by exo-effects with an area of 3619 μVs. The area of exo-effects for residual destruction above 450°C is 1356 μVs. In the TGA curve presented in Figure 5, the first stage of destruction covers the range from 20 to 300°C. At this temperature range, a smooth release of highly volatile components occurs, accompanied by a change in the aggregative state of the sample under study. The mass loss in this temperature range is 16.42%. The inflection of the DTA curve in this temperature range occurs at a temperature of 109.3°C. The inflection is accompanied by endo-effects up to the specified temperature and exo-effects above the specified temperature. The heat absorption area is 3854 μVs, and the heat release area is 2402 μVs. From 300 to 400°C, destruction begins to deepen, weight loss is 21.62%. The main destruction begins at 421°C, and then progresses to 448°C, the inflection occurs at a temperature of 438°C and ends at 475°C. The weight loss is 43.85%. The inflection in the DTA curve corresponding to this stage of destruction is observed at a temperature of 242.2°C with a corresponding endo-effect area of 2799 μVs. Residual destruction occurs from 500 to 580°C, at which the weight loss is 11.03%. This period of high-temperature destruction is accompanied by a large area of exo-effects of 7344 μVs, which is reflected in the DTA curve of the sample under study. As is evident from TGA curve shown in Figure 6, the mass loss is 7.43% up to 200°C that proves very weakness of the destruction. From 200 to 380°C, weight loss is 16.56%, that characterizes the first stage of destruction. The main destruction begins at 400°C, deepens at 430°C and ends at 470°C. The weight loss is 55%. Residual destruction occurs above 500°C at which the weight loss is 8.22%. In the DTA curve of the sample under study, the first inflection is observed at a temperature of 109.3°C. The area of endo-effects before the indicated temperature is 3854 μVs, the area of exo-effects after the indicated temperature is 2402 μVs. The next inflection of the DTA curve is observed in the temperature range from 280 to 470°C, which is accompanied by exothermic effects with an area of 3295 μVs. Residual destruction on the DTA curve is accompanied by a fairly large area of exo-effects - 7911 μVs.

Table 1. Study of the effect of modified ONPFO on the qualitative properties of hydropurified diesel fuel

Properties	Hydropurified DF	DF + ONPFO modified with imidaz. in 1:1 mol.ratio of NPA:PEPA	DF + ONPFO modified with imidaz. in 2:1 mol.ratio of NPA:PEPA	DF + ONPFO modified with imidaz. in 3:1 mol.ratio of NPA:PEPA
Thermal-oxidative stability, amount of the sediment, mg/100 ml	2.5	0.2	1.0	0.3
Cloud point, °C	-5	-5	-4	-10

Freezing point, °C	-10	-16	-14	-18
Cetane number (calculated)	49.63	48.42	48.80	48.74
Density, kg/m^3 at 20°C	837.3	841.06	839.87	840.05
Kinematic viscosity, mm^2/sec at 20°C	4.866	4.946	4.906	4.966

Considering the aforementioned, we can say that imidazolinamine-modified ONPFO have a fairly high thermal stability that makes them suitable for use as additives for fuels applied in internal combustion engines.

Thermal-oxidative stability of hydropurified diesel fuel with the addition of 0.004% synthesized additives was studied on LSART apparatus at 120°C during 4 hours in the presence of copper plates. A single-cylinder UTD-3 engine was used for the purpose of determining the ignition delay cycle of diesel fuel. The obtained research data and some other properties of diesel fuel are set into Table1.

As is known, the amount of sediment in hydropurified diesel fuels should not exceed 2.5 mg/100 ml according to the EN ISO 12205 standard. As is evident from the data given in Table 1, addition of imidazolinamine-modified ONPFOs to hydropurified diesel fuel causes a decrease in the amount of sediment from 2.5 to 0.2 mg/100 ml of product and proves the high thermal-oxidative efficiency of the synthesized additives. It is also noteworthy to point out the fact that the smallest amount of sediment was observed in the diesel fuel sample containing ONPFO, modified with imidazolinamine, synthesized in a 1:1 molar ratio of acid to polyamine, respectively.

Depressor properties of diesel fuel with the addition of synthesized additives were also positive. Thus, freezing temperature decreases from -10 to -18. In this case, on the contrary, the lowest freezing temperature is observed for a sample of diesel fuel containing ONPFO modified with imidazolinamine, synthesized in a 3:1 molar ratio of acid to polyamine, respectively.

The change in cetane number is not so remarkable; there is a slight decrease with a difference of one point. Kinematic viscosity remains within normal limits. Density properties vary in the range of 839-841 kg/m^3, slightly exceeding that of diesel fuel without additives.

Thus, it may be concluded that the use of ONPFO modified with imidazolinamines in the composition of hydropurified diesel fuel improves some of its performance properties, which will have a beneficial effect on the operation of the fuel in the engine.

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