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THE APPLICATION OF AMINO – AND HYDROXYETHYL IMIDAZOLINES OF PETROLEUM ACIDS AS MULTIFUNCTIONAL ADDITIVES FOR DIESEL FUEL

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ABSTRACT

In this research, the influence of amino- and hydroxyethylimidazolines of petroleum acids on the antistatic property and lubricity of diesel fuel has been studied. The researches illustrated that when the boiling point of petroleum acid fractions increases, the influence of imidazolines on the antistatic property and lubricity of diesel fuel decreases. Besides, it has been known that, the influence of aminoethylimidazolines of petroleum acids on the antistatic property and lubricity of diesel fuel is better than the influence of hydroxyethylimidazolines, On the other hand, it has been revealed that, when imidazolines of petroleum acids are added to the diesel fuel, the antistatic effect increases over time.

Indexing terms/Keywords

Diesel fuel; petroleum acids; imidazoline; antistatic effect; lubricity

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INTRODUCTION

Nowadays there are miscellaneous complex procedures for obtaining environmentally friendly diesel fuels and the most widespread procedure is to decrease the compounds which contain sulfur, nitrogen and polycyclic aromatic hydrocarbons as a result of hydrogenation process of diesel fuels [1-3].

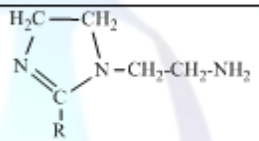
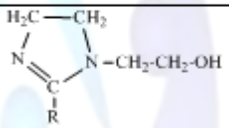
Despite this, reducing the amount of the heterocyclic compounds decreases the lubricity and antistatic effect of the fuel, therefore the details of the engine decay early and an instant spark causes ignition during the high-speed transference of fuel [4.5].

Currently, a number of additives are used for increasing the lubricity and electrical conductivity of the hydrotreated diesel fuels. These additives are the organic compounds which contain different functional groups (-OH, -COOH, -NH2, -NO2 and etc.) [6-10].

Nonetheless, it is clear that petroleum acids (PA) and their derivatives are applied to diesel fuel as additives for resource saving and improving some quality properties (lubrication, antistatic, anticorrosion and etc.) [11-14].

In this work, the influence of amino- and hydroxyethylimidazolines which were synthesized on the basis of natural PA fractions boiling in the range 140 – 160ºC, 160 – 180ºC and 180 – 200ºC to the lubricity and antistatic property of diesel fuel is studied (Table 1).

Table 1.The structure of amino- and hydroxyethylimidazolines which are obtained on the basis of different fractions of PA.

Fraction of PA.	Type of Imidazoline	Structure of Imidazoline	Conventional sign of Imidazoline.
140-160 ºC	Aminoethyl		PA I frAminoEIm
160-180 ºC			PA II frAminoEIm
180-200 ºC			PA III frAminoEIm
140-160 ºC	Hydroxyethyl		PA I frHydroxyEIm
160-180 ºC			PA II frHydroxyEIm
180-200 ºC			PA III frHydroxyEIm

2. Experimentals

2.1 Materials and methods

The petroleum acid fractions which were used for the research process have been obtained from HeydarAliyev Baku Oil Refinery of Azerbaijan; diethyltryamine (DETA) and N-Hydroxyethylendiamine (HEEDA) have been obtained from the "Sigma-Aldrich" company of Germany.

Imidazolines [17] were synthesized by the methods shown in the research.

The influence of imidazolines on the lubricity of diesel fuel has been investigated in the HFRR apparatus according to CEC F-06-A-96 method. In the tests, the temperature was 60˚C and the volume of used fuel samples were 2 ml. The efficiency of the fuel lubricity was evaluated with photomicroscope by measurement of wear scar diameter (WSD) of balls.

The specific electrical conductivity (SEC) which characterizes the antistatic property of diesel fuel has been determined by the apparatus EL - 4M according to GOST 25950.

The physical and chemical properties of diesel fuel which was used during the research are given in Table 2.

As can be seen from Table 2, the diesel fuel does not meet the requirements for lubricity (WCD ≤ 460 μm) and for specific electrical conductivity (SEC ≥ 150 pS/m). For investigating the influence of imidazolines on the lubricity and antistatic property of diesel fuel, they have been added to diesel fuel at the interval of certain concentration.

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Table 1.Physical and chemical properties of diesel fuel used in the research.

Properties of Diesel Fuel	Index of Diesel Fuel	Testing Method
Cetane number	47	ISO 5160
Density at °C kg/m3	849.5	ISO 12185
Kinematic viscosity, mm^2/s at 20°C	2.23	ISO 3104
Acidity, mg KOH/100 cm^3 of fuel	0.01	ISO 7537
Fractional composition, °C		
Initial boiling point	190	ISO 3405
10%	210	ISO 3405
50%	270	ISO 3405
90%	335	ISO 3405
96%	345	ISO 3405
Ignition temperature, °C	73	ISO 2719
Hydrocarbon composition, %		
Aromatic	21.23	ASTM D-6591
Paraffin - Naphthene	78.52	ASTM D-6591
Unsaturated	0.25	ASTM D-6591
Total Sulfur Content, % mass	0.0012	ASTM D-5453
Freezing point, °C	-36	
Cloud point	-28	ISO 116
The amount of water, %	-	
Lubricity,µm (average value)	620	ISO 12156
Flash point, °C	4	ISO 6297

3.RESULTS AND DISCUSSION

3.1 The analysis of antistatic property

The influence of aminoethylimidazolines of PA on the antistatic property of diesel fuel is shown in Fig. 1.

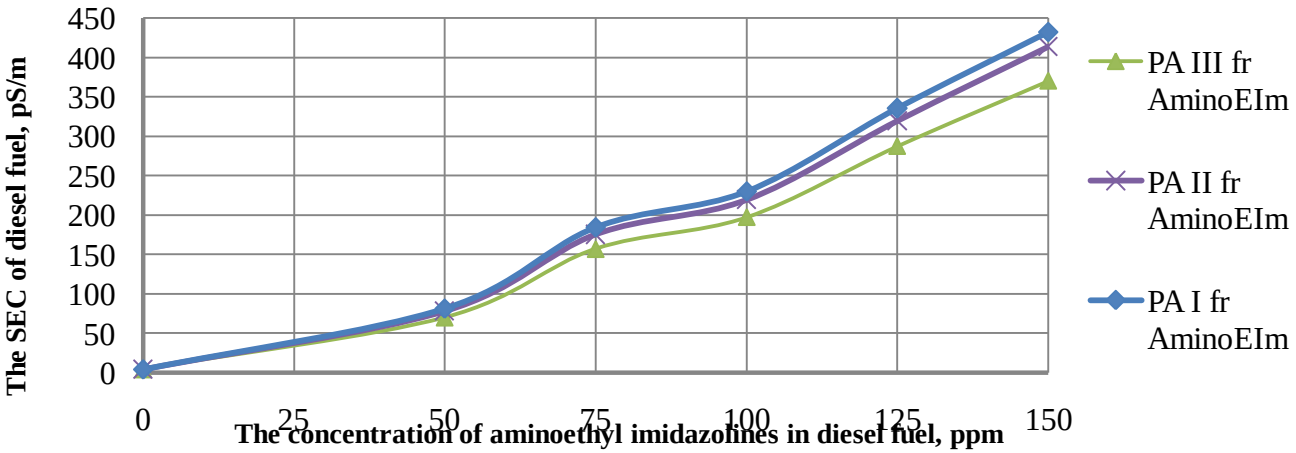

Fig.1. The effect of aminoethylimidazolines of PA on the antistatic property of diesel fuel.

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According to Fig. 1, it is revealed that, addition of aminoethylimidazolines of PA causes an increase in the antistatic property of diesel fuel. As can be seen from results, SEC was 81, 78 and 70 pS/m if the concentration of the aminoethylimidazolines of I, II and III fractions of PA was 50ppm, however, when the concentration was increased to 150ppm, SEC was also increased to 432, 413 and 370 pS/m respectively.

Besides, the value of SEC was changed between the interval of 171-184 pS/m of all fractions at the 75 ppm concentration of aminoethylimidazolines in the diesel fuel and it was above the minimum requirement (SEC > 150 pS/m) for antistatic effect. On the other hand, it was observed that, when the boiling point of imidazoline fractions increases, the antistatic effect decreases.

The influence of hydroxyethylimidazolines of PA on the diesel fuel is shown in Fig. 2.

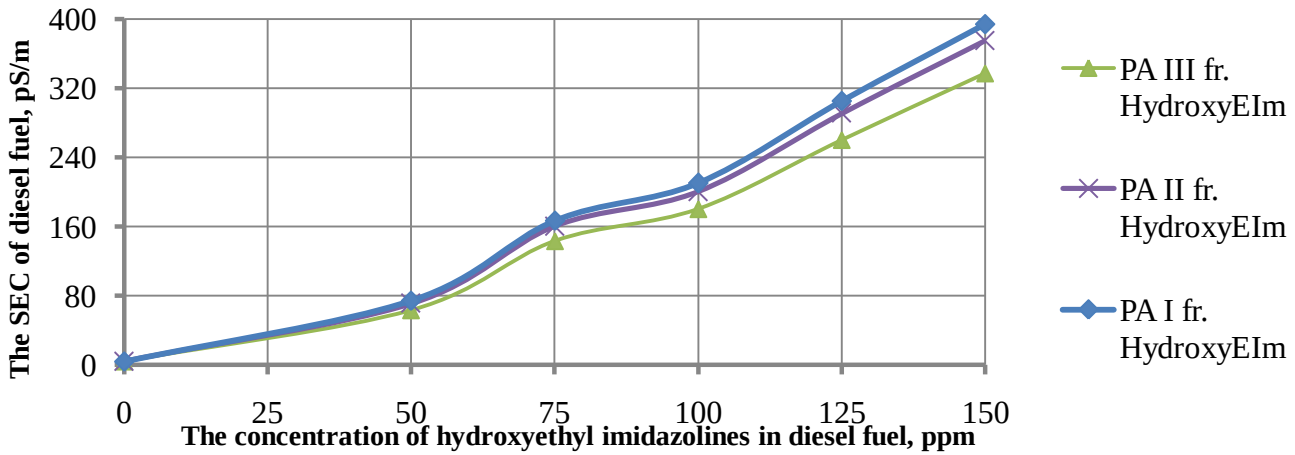

Fig.2. The influence of hydroxyethylimidazolines of PA on antistatic property of diesel fuel.

The results (Fig. 2) illustrate that, like aminoethylimidazolines of PA, the influence of hydroxyethylimidazolines on SEC of diesel fuel is directly proportional to the concentration of them in diesel fuel. As can be seen from the curves, I fraction has the highest antistatic effect (394 pS/m), while III fraction of hydroxyethylimidazoline has the lowest antistatic effect (337 pS/m). Antistatic effect is decreasing from I fraction to III fraction of hydroxyethylimidazolines like aminoethylimidazolines. Furthermore, the results show that, the minimum concentration limit of I and II fractions was 75 ppm for meeting the requirements for antistatic effect of diesel fuel, however, this concentration limit for III fraction of hydroxyethylimidazolines was 100ppm.

During the researches, it was discovered that, the effect of imidazolines of PA on the antistatic property of diesel fuel is dependent on the storage life of diesel fuel as well. It was observed that, the antistatic effect of imidazoline containing diesel fuel increases over time.

Taking into account of this, the SEC of amino- and hydroxyethylimidazolines of natural PA containing diesel fuels were measured at the first day of the addition of additive and after 30, 45, 60, 75 and 90 days. The results are shown in Table 3.

Table 2.The influence of storage life of diesel fuel on the SEC of amino- and hydroxyethylimidazolines of PA.

The storage life of fuel.	The SEC of aminoethylimidazolines of PA, pS/m				The SEC of hydroxyethylimidazolines of PA,, pS/m			
	gen.fr	I fr.	II fr.	III fr.	gen. fr.	I fr.	II fr.	III fr.
The first day	74	81	78	70	68	74	71	63
After 30 days	111	121	116	104	101	111	106	94
After 45 days	149	161	155	139	134	148	141	125
After 60 days	187	202	193	173	169	185	177	157
After 75 days	208	226	217	194	189	207	198	176
After 90 days	211	234	224	201	197	215	205	182

According to the researches, when 50 ppm aminoethyl and hydroxyethylimidazolines of PA are added to diesel fuel, it does not meet the requirements for the antistatic effect at the first day, however over time its antistatic effect increases. As can be seen from Table 3, the increment in antistatic effect of diesel fuel is different depending on the fraction composition of PA and type of imidazoline. So, the antistatic effect (161 pS/m and 155 pS/m) of diesel fuel which contains 50 ppm of aminoethylimidazolines of I and II PA fractions meets the requirements after 45 days, however the antistatic effect (157 pS/m and 173pS/m) of the imidazolines of III fraction reaches this requirement after 60 days. Despite this, the results show that, diesel fuel which contains 50 ppm of hydroxyethylimidazolines of PA meets the requirements for the antistatic effect (157-185 pS/m) after 60 days.

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3.2 The analysis of lubricity

The influence of aminoethylimidazolines of PA on the lubricity of diesel fuel is illustrated in Fig. 3.

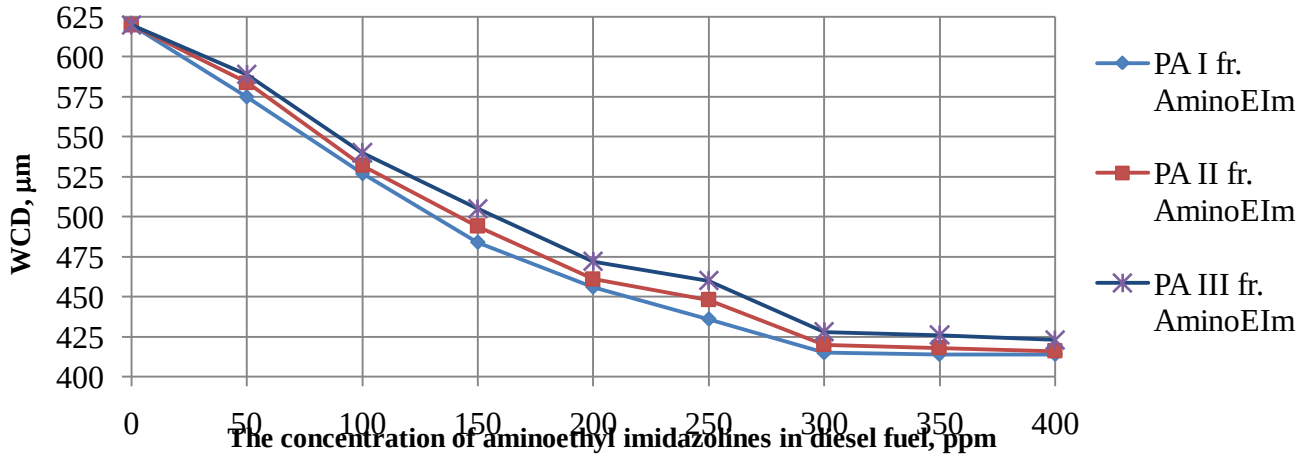

Fig.3.The influence of aminoethylimidazolines of different PA fractions on the lubrication quality of diesel fuel.

As can be seen from Fig. 3, while the concentration of imidazolines in diesel fuel increases, the lubricity of it increases as well. So, when the concentration of PA I frAminoEIm, PA II frAminoEIm and PA III frAminoEIm in the diesel fuel is 50 ppm, the WCD is 575, 584 and 589 µm respectively. When the concentration of imidazolines is increased to 250 ppm, WCD decreases to 436 µm for PA I frAminoEIm, 448 µm for PA II frAminoEIm and 460 for PA III frAminoEIm. As can be seen from the results, the value of WCD is below 460 µm when the concentration of PA I frAminoEIm is 200 ppm and the concentration of PA II frAminoEIm and PA III frAminoEIm is 250 ppm in diesel fuel.

In Fig. 4, the influence of hydroxyethylimidazolines of PA fractions on lubrication quality of diesel fuel is illustrated.

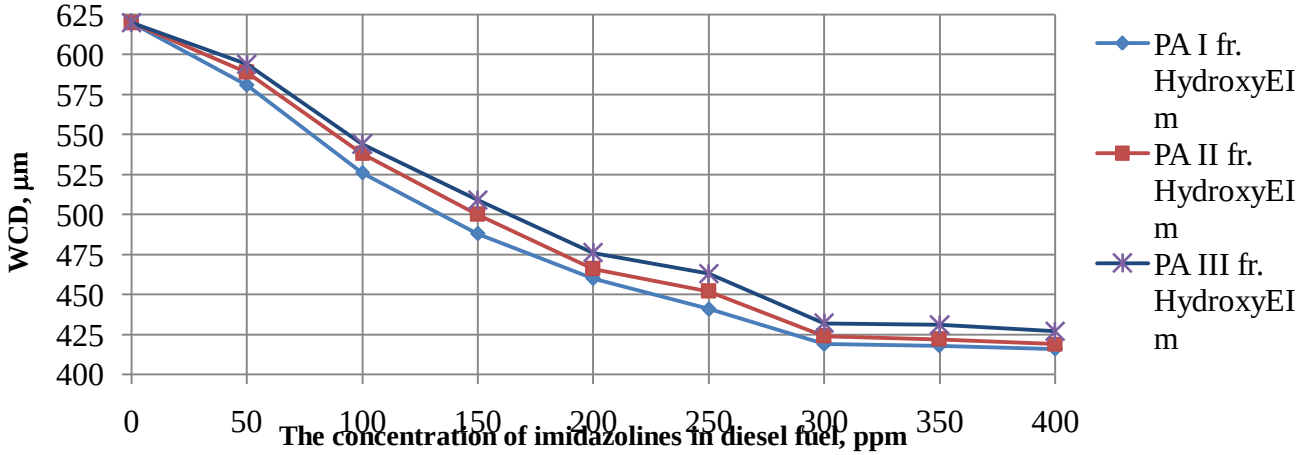

Fig.4.The influence of hydroxyethylimidazolines of different PA fractions on the lubrication quality of diesel fuel.

As can be seen from Fig. 4, while the concentration of hydroxyethylimidazolines in diesel fuel increases, the lubrication quality of it increases like aminoethylimidazolines of natural PA.

So, when the concentration of PA I frHydroxyEIm, PA II frHydroxyEIm and PA III frHydroxyEIm in the diesel fuel is increased from 50 ppm to 300 ppm, WCD is decreased from 581 µm to 419 µm for PA I frHydroxyEIm, from 589 µm to 424 µm for PA II frHydroxyEIm and from 594 µm to 432µm for PA III frHydroxyEIm.

As can be seen from the results, the normal concentration is 200 ppm for PA I frHydroxyEIm, however, it is 250 ppm for PA II frHydroxyEIm and PA III frHydroxyEIm. Normal concentration of imidazoline is a concentration at which the lubricity meets the requirements. Besides, as can be seen from the graph, the maximum concentration limit, at which the imidazolines affect the lubricity of diesel fuel is 300 ppm. Above this concentration limit, a broad change is not observed in the lubrication property of diesel fuel.

4. CONCLUSION

According to the results, aminoethylimidazolines of PA has a better antistatic effect and lubricity than hydroxyethylimidazolines. This is because the electrons of $–NH_2$ group are more fickle than the electrons of –OH group, the electronegativity of nitrogen is less than the electronegativity of oxygen and it can easily participate in the increase of SEC of fuel.

Besides that, the influence of imidazolines of PA on the antistatic property and lubricity of diesel fuel increases in the series of I fr.→II fr.→III fr. This is because, when the boiling point of PA increases, the molecular mass of acid radicals which are connected to carboxyl group also increases, since PA is monobasic acid. As a result of this, the amount of polar groups per unit decrease for both acids and their imidazolines, that is why their antistatic effect decreases.

Furthermore, amino- and hydroxyethylimidazolines of different PA fractions can be used as additives to diesel fuel for increasing both antistatic effect and lubricity. On the other hand, these additives are added to diesel fuel without any other solvent and the SEC of diesel fuel increases over time and this is the other advantage of these additives.

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