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NEW FORMULATION OF ALKYLPHENOLATE LUBRICANT'S ADDITIVES BASED ON NITROGEN, SULFUR AND CARBOXYLATE GROUP

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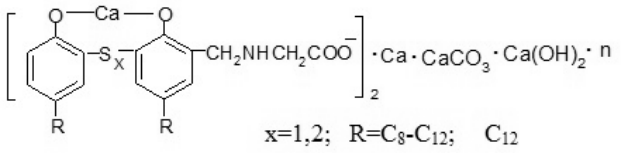
On the basis of simply found substances, easy methods to obtain new alkylphenolate additives containing different heteroatoms and functional groups, which are not described in the literature, were developed. There were synthesized medium-alkaline alkylphenolates containing such heteroatoms as nitrogen, sulfur and carboxylic group by aminomethylation and thiomethylation of methylene-bis- and thio-bis-alkylphenols, and alkylphenolates with alkalinity of 160-170 mg KOH/g, on the basis of neutralization with an excess $Ca(OH)_2$ and carbonate formation. Formaldehyde, benzotriazol, aminoacetic acid, diethanolamine and mercaptoacetic acid were used in the condensation reactions.



Structure of alkylphenolates containing N, COO−, N, S, COO−group obtained both with participation of aminoacetic acid, and methylene-bis- as well thio-bis-alkylphenol was studied by IR spectra from condensation to neutralization.
In comparison with such industrial additives as VNIINP-714, OLOA-218A, synthesized high alkaline AKI-150, AKI-215, AKI-218, AKI-223 additives had a high level of corrosion and oxidation resistance properties. AKI-150 and AKI-223 additives were a bit better on oxidation resistance and detergent properties comparing with both above mentioned industrial additives. Presence of such hetero atoms as nitrogen, sulfur and carboxylate group in the composition of the obtained additives provides the indicated properties.
On the basis of obtained additives and small concentrations of auxiliary additives, V,Q, D, (oil group abbreviations in Russian) group engine oils were prepared with high anticorrosive, antioxidant, antiwear and detergent properties. These oils met modern requirements and they were not worse than Shell's similar lubricating oils and Russian industrial analogues.

INTRODUCTION

Creation of new engines and technical equipments is faced with continuously growing requirements related to their exploitation. The main requirement for lubricating oils is endurance and better quality in harsh environments. In order to create modern engine oils, it is important to develop effective additives with wide range of exploitation properties. The main representative of these additives is multifunctional alkylphenolate additives.[1-7]

Searching, synthesizing and studying functional properties of new modifications of the indicated additives are the topical problems of petrochemistry.

Taking into account this, the goal of the research was synthesis of new multifunctional alkylphenolate additives containing calcium salts with N,S- heteroatoms, carboxylic group and study of these heteroatoms and functional groups impact on the lubricants oxidation, corrosion, wear resistance and detergent properties and creation of high-quality motor oil compositions on the base of the obtained additives.

EXPERIMENTAL

Thus, studies were conducted in the following areas:

Synthesis of nitrogen, sulfur heteroatoms, carboxyl, hydroxyl groups containing derivatives of alkylphenols;

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Obtaining of medium-alkaline calcium salts of synthesized derivatives of alkylphenols with neutralization calcium hydroxide;

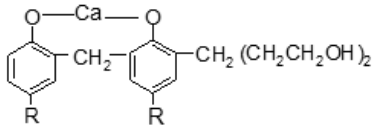
Synthesis of multi-functional and high alkaline additives on the basis of carbonation of the salts obtained by use of an excess calcium hydroxide with carbon dioxide;

Study of structure and functional properties of the synthesized additives by physicochemical methods;

Creation and application of different motor oil compositions for petrol and diesel engines on the basis of base lubricating oils and the synthesized additives.

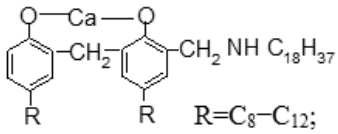
New alkylphenolate additives containing nitrogen and nitrogen carboxylate

In the synthesis of these alkylphenolate additives there were used methylene-bis-alkyl phenols, which were obtained on the basis of alkylphenols with para-substituted C_8-C_{12}, C_9 and C_{12} radicals. The noted alkylphenols were condensed with formaldehyde at a temperature of 45-55^{0}C in the presence of $Ca(OH)_2$ as catalyst (0.3-0.5%) and the course of the reaction was controlled by refraction index (n_D^{20}). Methylene-bis-alkylphenols were condensed with formaldehyde (33-35% aqueous solution), in certain cases paraform and various nitrogen compounds (diethanolamine, octadecylamine, alkenylsuccinimide, aminoacetic acid, benzotriazol)[8-11]. As a result of neutralization of the obtained product with calcium hydroxide, new alkylphenolate additives containing nitrogen and nitrogen-carboxylate were synthesized. All additives are obtained on the basis of industrial products in water-oil medium. At the end, the product is separated from water by drying and released from admixture by centrifuger. Thus, here it is given the supposed formulas of the obtained additives to the lube oils as a basic product of the synthesis.



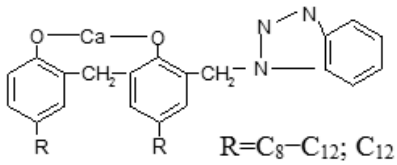
R=C_8–C_{12}; C_{12};

AKI-211–calcium salt of condensation product of methylene-bis-alkylphenol with diethanolamine and formaldehyde



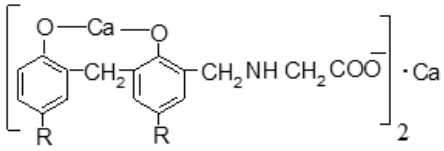
R=C_8–C_{12};

AKI-212 –calcium salt of condensation product of methylene-bis- alkylphenol with octadecylamine and formaldehyde



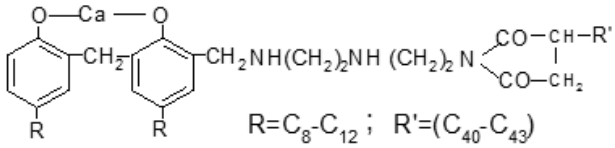
R=C_8–C_{12}; C_{12}

AKI-208–calcium salt of condensation product of methylene-bis- alkylphenol with benzotriazol and formaldehyde



R=C_8–C_{12}; C_9; C_{12}

AKI-140–calcium salt of condensation product of methylene-bis-alkylphenol with aminoacetic acid and formaldehyde



R=C_8-C_{12} ; R'=(C_{40}-C_{43})

AKI-214- calcium salt of condensation product of methylene-bis-alkylphenol with alkenyl succinimide and formaldehyde

Nitrogen-sulfur, nitrogen-sulfur-carboxylate and sulfur-carboxylate containing alkylphenolate additives

As the first stage of obtaining these additives, sulfurization of alkylphenol was conducted. The process of sulfurization of alkylphenol was implemented with participation of different catalysts (the amount of catalyst is indicated in accordance with alkylphenol): NaOH–0.5-0.6%, 3.2% monoethanolamine + 0,49% $Ca(OH)_2$ [12] are an optimal.

For the sulfurization of alkylphenol process, the following optimal conditions were chosen:

- conducting the reaction in nitrogen gas atmosphere;
- temperature range: 150-188^{0}C;
- duration: 4.0 – 4.5 hours

The amount of sulfur in the sulfurized alkylphenol, obtained as a result of the reaction conducted in this optimal condition was 3.9-4.3%.

Nitrogen-sulfur and nitrogen-sulfur-carboxylate containing alkylphenolate additives were synthesized by aminomethylation of alkylphenols with compounds containing formaldehyde, amine and amine carboxylate group and neutralization of the obtained product with calcium hydroxide.

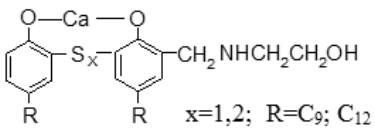
$$2\,RC_6H_4OH + S_8 \xrightarrow[-H_2S]{kat.} HO(R)C_6H_3S_x\,C_6H_2(R)OH$$

x=1; 2 R=C_8 – C_{12}, C_9, C_{12};

Aminomethylation reaction of the sulfurized alkylphenols was conducted at a temperature of 65-90^{0}C during 0.5-2.5 hours depending on amine compound.

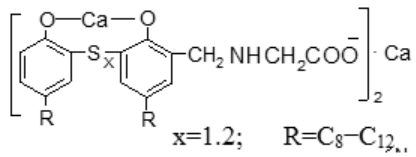
Sulfur-carboxylate containing alkylphenolate additives were synthesized as a result of condensation of methylene-bis-alkylphenol with formaldehyde and mercaptoacetic acid and neutralization of the obtained product with calcium hydroxide.

Nitrogen-sulfur, nitrogen-sulfur-carboxylate and sulfur-carboxylate based new alkylphenolate additives were synthesized according to the noted reaction scheme with the following expected formulas:



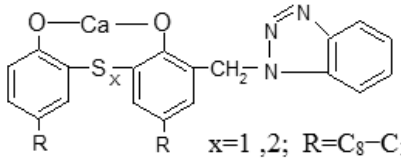
x=1,2; R=C_9; C_{12}

AKI-216 - calcium salt of condensation product of sulfurized dodecylphenol with monoethanolamine and formaldehyde



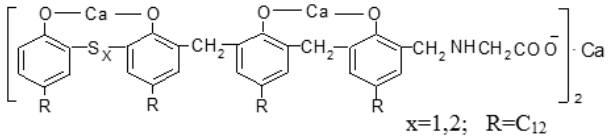
x=1.2; R=C_8–C_{12}, C_{12}

AKI-204 - calcium salt of condensation product of sulfurized alkylphenol with aminoacetic acid and formaldehyde



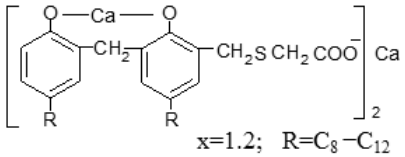
x=1 ,2; R=C_8–C_{12}; C_9

AKI-209 - calcium salt of condensation product of sulfurized alkylphenol with benzotriazol and formaldehyde



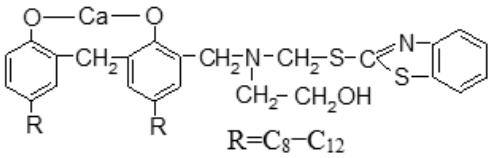
x=1,2; R=C_{12}

AKI-222- calcium salt of processing of mixed condensation product of sulfurized alkylphenol and methylene-bis-alkyl-phenol with formaldehyde and amino acetic acid with formaldehyde



x=1.2; R=C_8–C_{12}

AKI-147- calcium salt of thiomethylation product of methylene-bis-alkylphenol with mercaptoacetic acid and formaldehyde



R=C_8–C_{12}

AKI-217- calcium salt of condensation product of methylene-bis-alkylphenol with monoethanol-amine, captaks and formaldehyde

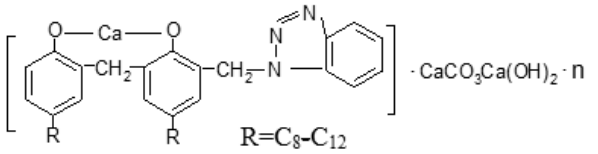
High alkaline multifunctional alkylphenolate additives

Alkalinity is the most important indicator stipulating neutralizing, dispersive, surface activity, adsorption, solubilization properties and even characterizing the level and depth of all exploitation properties of alkylphenolate additives.[5, 19-22]

In the synthesis of high alkaline additives calcium hydroxide used in the neutralization doesn't make 20% of alkylphenol, the considered amount is 2, 3, 4 times more and carbonation is carried out with proper amount of CO_2 gas. These additives are used in preparation of lubricating oils for various industrial, transport and ship diesel engines. High alkaline additives with $CaCO_3$ in the center and hydrocarbon molecules-neutral alkylphenolates and carboxylates located on the periphery, having colloidal structure, are qualitative modifications with alkalinity which is 2-2.5 times higher than medium alkaline salts.

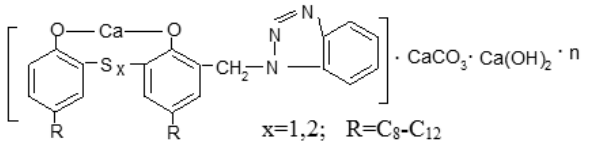
The main stage in the synthesis of high alkaline additives is carbonation process. The main factors are the amount of calcium hydroxide, the amount of CO_2 gas, feed rate, absorption temperature and duration, the amount of water involved in the reaction, chemical composition and amount of used promotor.

Below there are formulas of high alkaline additives synthesized on the basis of condensation products of the medium alkaline salts obtained in the optimal conditions determined by t AKIng into account these factors:



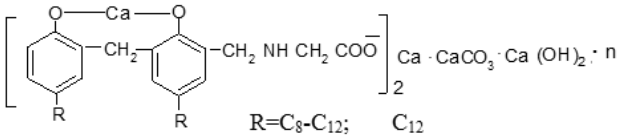
R=C_8-C_{12}

AKI-215- carbonated calcium salt of condensation product of methylene-bis- alkylphenol with formaldehyde and benzotriazol



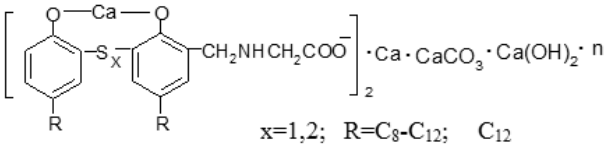
x=1,2; R=C_8-C_{12}

AKI-218- carbonated calcium salt of condensation product of sulfurized alkyl-phenol with formaldehyde and benzotriazol



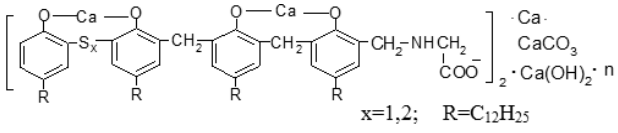
R=C_8-C_{12}; C_{12}

AKI-150- carbonated calcium salt of condensation product of methylene-bis- alkylphenol with formaldehyde and aminoacetic acid



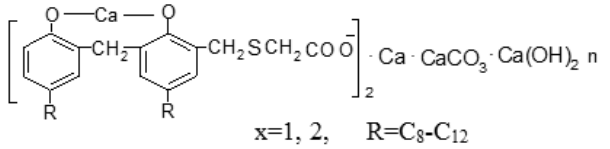
x=1,2; R=C_8-C_{12}; C_{12}

AKI-224 - carbonated calcium salt of condensation product of sulfurized alkylphenol with formaldehyde and aminoacetic acid



x=1,2; R=$C_{12}H_{25}$

AKI-223-carbonated calcium salt of condensation product of the compound (condensation product of sulfurized alkylphenol with formaldehyde and methylen-bis-alkylphenol) with formaldehyde and aminoacetic acid



x=1, 2, R=C_8-C_{12}

AKI-157- carbonated calcium salt of thiomethylation product of methylen-bis-alkylphenol with mercaptoacetic acid and formaldehyde

Temperature and CO_2 gas feed rate are factors influencing on carbonation. CO_2 gas feed rate in additives containing nitrogen-sulfur is 28-33mL/min.

RESULTS AND DISCUSSION

In the IR spectrum of the sulfurized nonyl phenol obtained as a result of the reaction conducted in this optimal condition, absorption bands of −C−S− bond was observed in 620-625 cm^{-1} and a weaker absorption bands characterizing −S−S− disulfide bond in 550 cm^{-1} area. In the IR spectrum of the sulfurized dodecylphenol these bands were accordingly observed in 619-620 cm^{-1} and 468-470 cm^{-1}. Availability of sulfurized alkylphonolate additives –C−S− and –S−S−groups in molecules improves their functional features.

In IR spectrum of condensation product of AKI-140 and AKI-204 additives obtained with participation of aminoacetic acid there is observed a new absorption band in 1633-1636 cm^{-1}, it can be related to carboxylic ion.Valence vibrations belonging to N^+H_3 as wide intensive band appears in 3160 cm^1. As this band coincides with CH and OH groups, identification of N^+H_3 and N^+H_2 becomes more difficult. As a result of impact of the position of N^+H_2 ion in the molecule on $–COO^-$ ion, band characterizing carboxylate ion can be seen in 1636 cm^{-1} in IR spectrum of condensation product obtained from sulfurized alkylphenol and ordinary alkyl phenol. In the IR spectrum of amino acetic acid this band is observed in 1613 cm^{-1} because of N^+H_3 Fig.1 (a,b).

In the IR spectrum of neutralization product - calcium salt given in Fig. 2 NH-group of amino-acetic acid and NH group being empty from positive charge and originated from aminomethylation of alkylphenol (as N^+H_3 , N^+H_2) can be seen in 3431.98-3613.27 cm^{-1} and a large and intensive absorption band of COO− ion in 1593cm^{-1}. Sliding to another weaker area, may be the result of stronger carboxylic ionic bond (with calcium). In addition, the absence in the given spectrum of phenolic OH-ionic band which is clearly observed in the condensation product and observation of metal-carboxylate ionic band in 1593cm^{-1}, confirm the formation of both phenolate and carboxylate at the same time. And the high alkalinity of the additive in comparison with ACK additive (1.5 times more), is a result of formation of two alkalinity centers in the synthesized additives. (phenolate and carboxylate**)** The similar situation is observed in the synthesis of AKI-140 additive. From the beginning of the process to its end there were observed differences between forms of carboxylate ionic bands. Each product obtained at every stage was washed and cleaned from mixes by centrifuge.

IR spectra were registered at Fourier-Nicolet IS-10 IR Spectrometer made in the US.

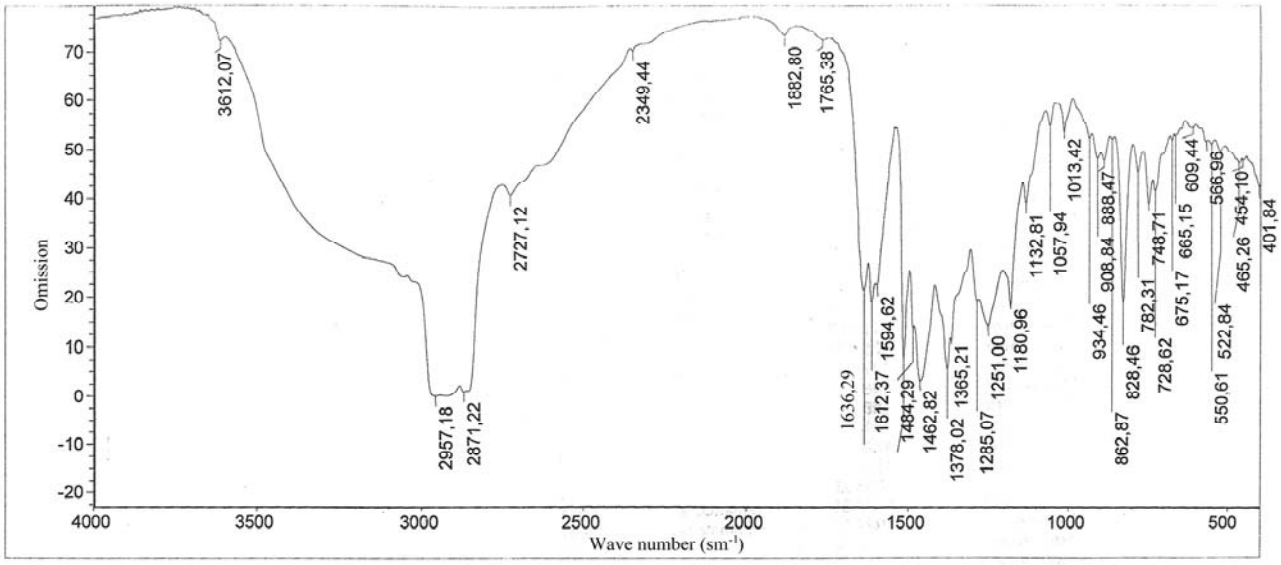


Fig. 1 (a) – IR spectrum of aminomethylation product of sulfurized dodecylphenol with aminoacetic acid.

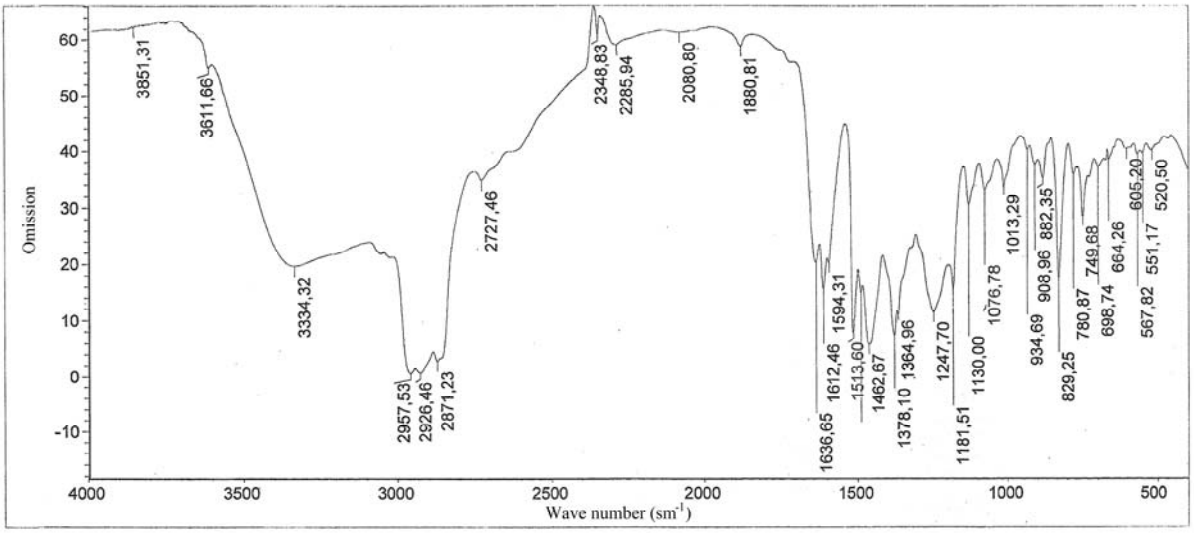


Fig. 1 (b) – IR spectrum of aminomethylation product of dodecylphenol with aminoacetic acid.

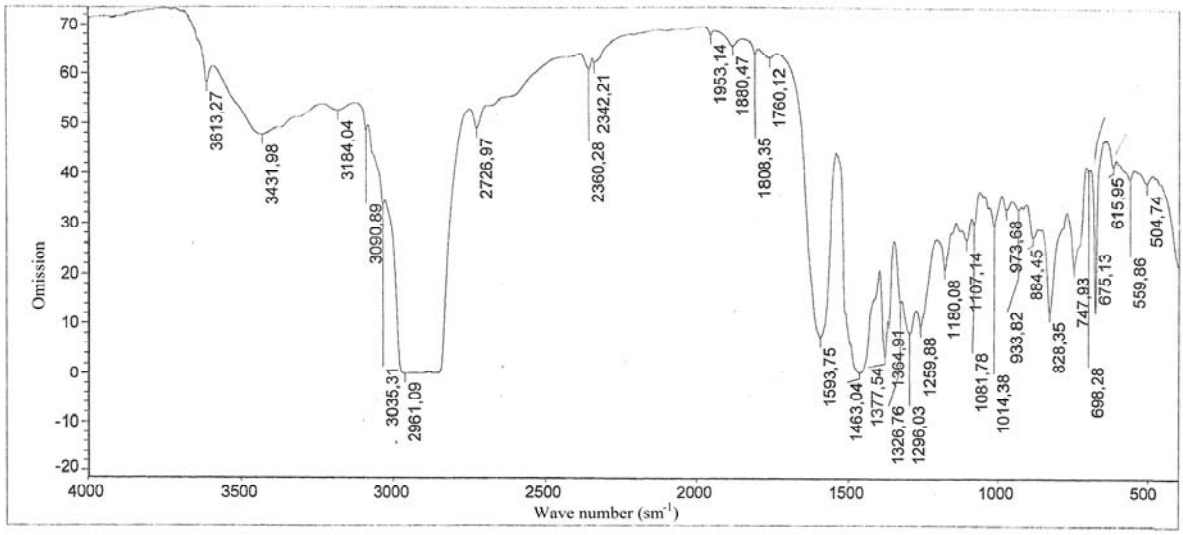


Fig. 2 – IR spectrum of AKI-204 additive (calcium salt).

The new modifications of synthesized alkylphenolate-type additive improve one or another functional property according to the chemical nature of amino component included in a molecule of additives. For example: AKI-140 alkylphenolate additive obtained on the basis of condensation of aminoacetic acid and formaldehyde improves oxidation, corrosion resistance and detergent properties; AKI-208 additive obtained on the basis of benzotriazol improves oxidation and corrosion resistance properties; AKI-214 additive obtained on the basis of alkenyl succinimide significantly improves detergent-dispersive properties.

Advantages of their analogues without nitrogen in comparison with methylene-bis alkylphenolate (*IXP-109 additives being calcium salt) are reflected in table 1 (a). It is obviously from the table. nitrogen containing new modifications significantly improve the main functional characteristics - corrosion, oxidation and wear resistance and detergent-dispersive characteristics.

So, wear diameter in oil without additive is 0.85-0.95 mm, in methylene-bis-alkylphenolates 0.65-0,70 mm, but in nitrogen containing one is 0.5-0.55 mm. Detergent properties of pure oil without additives and methylene-bis-alkylphenolate are 5.0-6.0 and 0.5-1.5 point accordingly, however the same indicator of the synthesized new modifications is 0.5 and AKI-214 additive is 0-0.5 point. [8-11]

Physicochemical and functional properties of nitrogen-sulfur, nitrogen-sulfur-carboxylate and sulfur-carboxylate based additives are given in table 1(b). As can be seen from comparative characteristics of the additives nitrogen-sulfur containing combined additives have better oxidation and wear resistance properties.[13-18]

Table 1

Physicochemical and functional properties of heteroatoms and functional groups containing alkylphenolate additives

Additive samples (with hetero-atoms and functional groups)	Kinema-tic viscosity, mm^2/s	Sulfate ash, %	Alkalinity, mgKOH/g	Composi-tion, %		M-8 oil with 5% additive			
				N	Ca	Corro-sion, (lead plates), g/m^2	Stability on in-duction period for sludge formation (by IPO, 30h.), sludge, %	Detergent property, point	Wear resistance, (wear spot diameter), mm
a) N containing alkylphenolates									
IXP-109*	70-75	8.5-9.2	70-75	–	–	6.9	0.85-0.90	0.5-1.0	0.65
AKI-211	75-90	9.5-11.0	109.5-114	0.76	2.4	2.5-3.4	0.15-0.3	0.5	0.55
AKI-212	81-90	6.7	71.57	0.85	2.1	2.3	0.25	0.5	0.53
AKI-214	69-107	6.8-7.2	71.5-77.6	0.73	2.4	2.0-3.0	0.15-0.35	0-0.5	0.50
AKI-208	75.2	7.9	5.8-8.5	1.92	2.7	0.1-0.8	0.11-0.18	0.5	0.48-0.5
AKI-140	82-88	9.8	95-105	0.74	2.7	1.5-3.0	0.2-0.25	0.5	0.52-0.55
b) N, S containing alkylphenolates				**S**	**Ca**				
TSIATIM-339(S) ** (ind. simp)	–	10,2	41,5	4.6	-***	35.6	3.5	1.0	–
AKI-147 (S,COOH)	85-95	9,6	88,0	1.35	2.25	3.6	0.45	0.5	0.38
AKI-209 (N,S)	82-87	8,2-9,0	87-95	2.3	2.7	0.8-0.9	0.03-0.06	0.5	0.38-0.40
AKI-204 (S,N,COOH)	79,1	9,2	98,6	2.3	2.75	1.8	0.21	0.5	0.38
AKI-222 (S,N,COOH)	78,0	9,1	95,9	1.2	2.6	1.4	0.23	0.5	0.42
AKI-217 (N,S)	68,5	10,5	128	1.25	3.0	5.1	0.2	0.5	0.36
ACK (COOH) (ind.simp)	65-80	6-8	50-60	–	–	40-50	0.8	0.5-1.0	0.60

* IXP (Institut Ximii Prisadok) (in Russian) - Institute of Chemistry of Additives
** TSIATIM (Tsentralniy Institut Aviatsionnikh Topliv i Masel) (in Russian) – Central Institution of Aviation Fuels and Oils,
*** Ba ≥ 4,7 – 5,0

On the basis of the results of the thermogravimetric analysis it was determined that, beginning temperature of alkylphenolate additives obtained from sulfurized alkylphenol was 30-35 ^{0}C higher in comparison with nitrogen containing ones.[12]

At studying dependence of corrosion and wear resistance indicators of AKI-208 additive calcium salt of aminomethylation product of methylene-bis-alkylphenol with benzotriazol and AKI-209 additive obtained on the basis of sulfurized alkylphenol, on concentration of the additives in M-8 oil, it was revealed that corrosion and wear resistance characteristics of both additives were very higher than analogues without nitrogen and sulfur - IXP-109 and AKI-115 additives accordingly.[15]

In curves 3 and 4 expressing corrosion resistance characteristics of AKI-208 and AKI-209 additives there are not observed significant differences at concentration of 3 and 5% (Fig. 3).

Thus, there were observed: in only nitrogen containing alkylphenolates - weak thermooxidation and wear resistance characteristics; in only sulfur containing alkylphenolates - weak corrosion resistance indicators; in nitrogen-sulfur containing ones - high level of multifunctionality.

Comparative functional indicators of obtained high alkaline additives and industrial analogues are given in Table 2. As can be seen from the indicators of the table introducing the separate hetero atoms (N, S) and the functional group (COOH) into the additive molecule provides their multifunctionality and high-quality. Additives synthesized by reason of their functional properties, in particular corrosion and oxidation re-

sistance, are better than industrial analogues.The obtained results allow to create a high group motor oils by use of synthesized additives.

AKI-215 and AKI-223 (it is slightly better than VNIINP -714) additives have the best corrosion and wear resistance accordingly.

AKI-223 and AKI-150 have higher oxidation resistance properties in M-14G_2 oil (Fig. 4, 5).[19-22]

The results of these studies show that synthesized new high alkaline additives containing N, S – heteroatoms and carboxylic group are often better than industrial analogues (VNIINP -714, OLOA-218, AMOKO-9230) due all indicators. The experimental additives have high water resistance. For example: water resistance of high alkaline AKI-150 and AKI-223 is higher than alkalinity of other synthesized alkylphenolate additives (reduction of alkalinity makes 6-8%).

A number of substances were used as promotor in the synthesis of high alkaline multifunctional alkylphenolate additives. It was determined that the best result was achieved by using ethylene glycol, glycerol, diethanolamine as promotor (the additives differed both by high alcalinity and functional properties).[10, 23-29]

Being accordingly calcium alkylsalicylate and high alkaline calcium alkylsalicylate ACK and MASK are industrial samples without heteroatoms.[28]

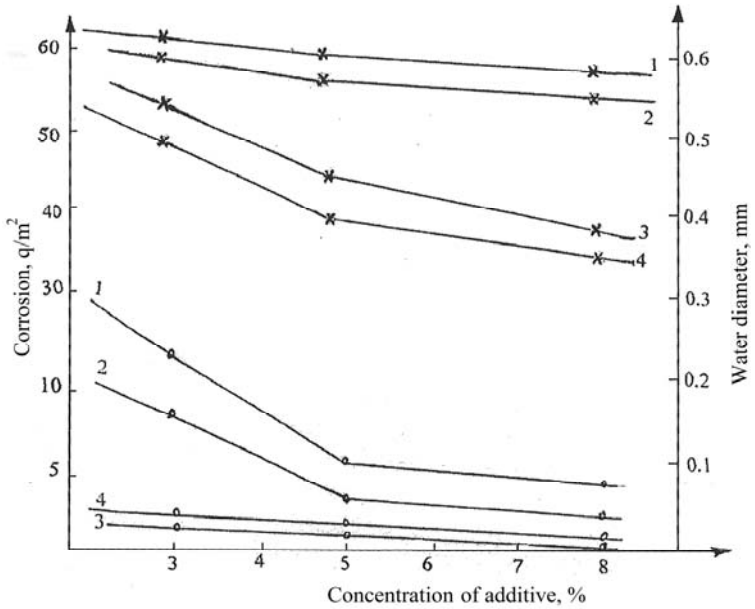


Fig. 3 – Dependence of wear and corrosion resistance of the additives on their concentration in M-8 oil 1-IXP-109, 2-IXP-115, 3-AKI-208, 4-AKI-209. --x----x----wear resistance ; ---o----o— corrosion resistance.

Table 2

Functional properties of heteroatom containing highalkaline alkylphenolate additives

Additives	Alkalinity mgKOH/g	M-8 oil with 4% additives			
		Corrosion (lead plates), g/m²	Stability on induction period of sediment formation (by IPO, 30 hour), sediment, %	Detergent property, point	Wear resistance, mm
AKI-215 (N)	153.0-155.0	0.1-1.0	0.11-0.3	0.5	0.48-0.50
AKI 218 (N,S)	155.0-160.0	0.1-0.7	0.06-0.08	0.5	0.35-0.40
AKI-224 (S,N,COOH)	174.0	1.9	0.3	0-0.5	0.39
AKI-150 (N,COOH)	150-170	0,7-1,2	0,1-0,25	0-0,5	0,48-0.50
AKI-223 (S,N-COOH)	190-200	1.5-2.1	0.23	0-0.5	0.40
AKI-157 (S, COOH)	140.0-160.0	1.0 -1.5	0.01-0.1	0-0.5	0.4
VNIINP-714(S) *	143-155,0	6.8	0,35	0,5	0,40
OLOA-218(S)	140-147	10.9	0,40	0,5	0,40
AMOKO-9230(S)	120	7.0	0.40	0.5	0.40
MASK(COOH)	140-160	6.9	0.65	0.5	0.6

* VNIINP (Vserossiyskiy Nauchno Isledovatelskiy Institut po nefte Pererabotke) in Russian – All-Russian Research Institute of Petroleum Refining.

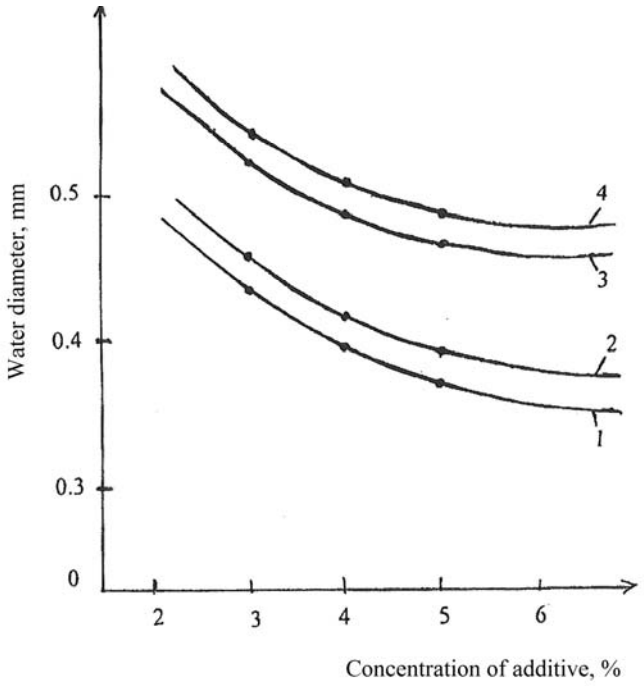


Fig. 4 – Dependence of wear resistance of M-8 oil on 3.5% concentration of the additive:
1. AKI-223, 2. VNIINP-714; 3. AKI-150, 4. MASK.

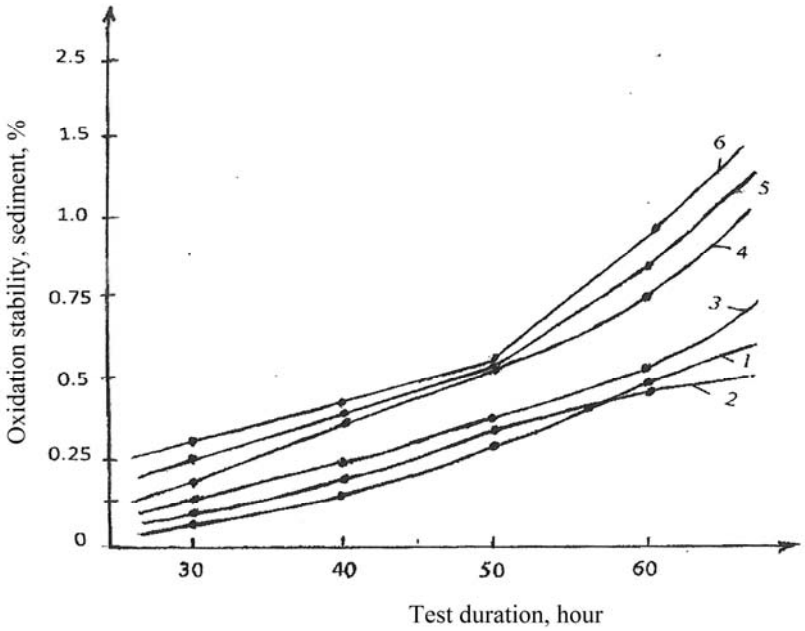


Fig. 5 – Dependence of the resistance of M-14G_2 oil to oxidation with 5% additive on oxidation test duration
1.AKI-150, 2.AKI-223, 3.AKI-218. 4. AKI-215, 5. VNIINP-714, 6. MASK.

By use of above mentioned additives universal motor oil M-8B for petrol and diesel engines, M-10G_2 for transport diesels, M-14G_2, M-14G_2к, M-16, IXP-3 for industrial, diesel locomotive and four-stroke transport diesels, M-12B_2, M-20Bp, M-20B_2Ф for ship diesels and other motor oils were developed and tested. It was established that functional properties – corrosion, oxidation, wear – resistance and detergent properties of oil samples met modern requirements and they were not worse than similar oils.[29, 31-33]

As example in tables 3 and 4 there are given indicators of M-8B and M-20Bp oils.

Numbers of GOST and ASTM methods used to define the parameters of physicochemical and functional properties of oils are given in tables. Tribological properties were studied on the four-ball machine (ChShM-4*) on GOST** 9490; ASTM 2266.

Table 3

Physicochemical indicators of M-8B motor oil with AKI-150 additive and comparative test results

Indicators	M-8B GOST-10541-78	M-8B oil with experimental AKI-150 additive		M-8B type Rimula C20W-20X-100 (Shel product)	Test method	
		I	II		GOST	ASTM
Kinematic viscosity, 100^0C, 0^0C, mm^2/s	8±0.5 ≤1200	8.48 -	8.5 1095	8.8	GOST 33	D 445
Viscosity index, not less than	93	94	96	102	GOST 25371	D2270
Alkalinity, mgKOH/g	4.0	6.84	6.8	4.0	GOST 11362	D4739
Sulfate ash, % , not more than	0.95	0.94	0.91	0.65	GOST 12417	D 874
Mass of mechanical mixtures, %	0.015	0.08			GOST 6370	–
The water weight,%	no	no	no	no	–	–
Flash point in an open pot, ^{0}C, not lower than	200	212	215	241	GOST 4333	D 92
Pour point,^{0}C no more than	Minus 25	Minus 26	Minus 27	Minus 25	GOST 20287	D 97
Detergent property, point	0.5	0	0	0.5	GOST 5726	–
Stability on induction period for sludge formation, (IPO, 30 hours sludge, %	30	35	35	30	GOST 11063	–
Corrosion (on CI and C2 type lead plates, GOST 3778-77) g/m^2, not more than	10	no	no	no	GOST 20502	D 665
Purity degree, mg, for 1000g oil , not more than	500	210	-	-	GOST 12275	–

ChShM- Chetiryokh Sharikovaya Mashina (in Russian) - Four-Ball Wear Test Machine
**GOST -Gosudarstvenniy Standart (in Russian) – State Standards

Table 4

Comparative test results of physicochemical indicators and functional properties of M-20Bp (lubricating composition with the experimental additives)

Indicators	M-20Bp oil ** TC 38.101593-86 (standard)	Known oil with AKI-114 additive (N containing)	New oil with AKI-218 additive (N, S containing)	Test method	
				GOST	ASTM
Kinematic viscosity, 100^0C, mm^2/s	19.5-21.5	20.12	21.02	33	D 445
Viscosity Index,	85	85	87	25371	2270
Alkalinity , mg KOH/g, not less than	2.7	3.0	3.2	11362	D 4739
Sulfate ash,%, not more than	0.9	0.79	0.72	12417	D 874
Flash point in an open pot, ^{0}C not less than	220	270	275	4333	D 92
Pour point,^{0}C, not more than	Minus 15	Minus 15	Minus 15	20287	D 97
Corrosion, (on CI and C2 lead plates, on GOST 3778-77) g/m^2, not more than	no	no	no	20502	D 665
Stability on induction period for sludge formation, (IPO, 35 hours) sludge, %	resistance (0.5)	no resistance 30 hours (0.5)	resistance 40 hours (0.3)	11063	–
Colour, TSNT unit *	not normalized , determination needed	8.0	8.0	20284	D1500-04a

Table 4 (continued)

Density, 20^0C, kg /m3, not more than	902	895	896	3900	D 4052
Detergent potential, 250^0C, %	–	90	95	10734	–
Detergent property, point	not normalized, determination needed	0.5	0	5726	–

[*] TSNT – kolorimetr dlya opredeleniya tsveta (in Russian) – Colorimeter for determination of colour
[**] Bp – Ship Diesel Oil Group in Russia

As can be seen from property indicators (corrosion, oxidation and wear resistance, detergent properties) of M-8B and M-20BP oils prepared by use of synthesized AKI-150 and AKI-218 additives (tab.3,4) they fully meet standards for motor oils.

CONCLUSIONS

The new additives (AKI-208, AKI-211, AKI-212, AKI-214, AKI-140) obtained by theinclusion of various nitrogen containing functional groups (diethanolamine, amine octadecyl, alkenyl succinimide, benzotriazol, aminoacetic acid, etc.) into alkylphenol molecule, along with strong detergent properties have high corrosion, oxidation and wear resistance indicators in comparison with analogues without nitrogen.

The inclusion of sulfur atom into nitrogen-containing modifications or the inclusion of nitrogen atom into sulfur-containing ones improve their oxidation, corrosion and wear resistance properties (AKI-204, AKI-209, AKI-217 and etc).

In oils prepared by use of additives obtained on the basis of Mannich Bases and reaction of nitrogen containing condensation product of sulfurized alkylphenol with mix composition there is observed improvement of the functional properties, including corrosion, oxidation and wear resistance and neutralizing, detergent properties, in comparison with additives containing one of these heteroatoms (AKI-140, AKI-147, AKI-222).

As a result of neutralization of medium alkaline alkylphenolate additives with excess calcium hydroxide and carbonation with carbon dioxide gas high alkaline (150-200 mgKOH/g) analogues were synthesized. Optimal conditions of carbonation process of alkylphenolate additives containing nitrogen and sulfur were studied, the feed rate of carbon dioxide gas is 25-35ml/min.

The best promotors of carbonation process among used ones such as ethylene glycol, glycerin, acetic acid there were ethylene glycol, glycerol and diethanolamine.

It was established that nitrogen-sulfur and carboxylate-containing AKI-223 additive had a high alkalinity (190-200 mg KOH/g).

For the first time, new multifunctional AKI-150 additive consisting of carbonated calcium salt of condensation product of methylene-bis-alkylphenol with formaldehyde and aminoacetic acid was obtained. In comparison with alkylsalicylates this additive contained nitrogen atom. It was been established that AKI-150 additive both individually and in various oil compositions was better by corrosion resistance properties than such foreign commercial additives as MASK, VNIINP-714 and OLOA-218.

The synthesized new multifunctional alkylphenolate additives containing various heteroatoms and functional groups were tested in M-8B oil for gasoline engines (transport, industry, ships) and in motor oils (M-10G_2, M-12B_2, M-14G_2, M- 14G_2к, M-16 IXP-3, M-20Bp, M-20V_2f) Russian Oil Groups for different types of diesel engines with the positive results and it was established that the exploitation properties of the experimental oils met modern requirements.

REFERENCES

1. S. V. Monin and T. V. Pavlova, *Chem. and Tech. of Fuels and Oils*, **1978**, *3*, 61–63.
2. R. D.Stauffer, US Pat. 4710308. Dec 1. **1987**.
3. T. C.Jao and C. K.Esche, US Pat. 4973411. Nov. 27. **1990**.
4. A.M. Guliyev, *Chem. and Tech. of Oil and Fuel Addit.*, **1985**, 230-231.
5. N. E. Seleznyova, A. Ya.Levin and S.V. Monin, *Chem. and Tech. of Fuels and Oils,* **1999**, *6*, 39–43.
6. W.R. Donovan and K. M.John, US Pat. 4157309. Jun 5. **1979**. Additive–Mannich Base.
7. C. John and H.G. Alan., Eng Pat.1581747. Dec 17. **1980**.
8. A.Kh. Mammadova, Az Pat I20062079, Aug 14. **2006**.
9. A.Kh. Mammadova, A.K. Kazimzadeh and B.I. Abdullayev, *Azerb. Oil Indust.*, **2009,** *7*, 60–62.
10. A. Kh.Mammadova, A.K. Kazimzadeh and E.A. Nagiyeva, *Oil Ref. and Petrochem*, **2010**, *9*, 28-29.

11. A.K. Kazimzadeh, E.A. Nagiyeva and A.Kh. Mammadova, *Azerb. Oil Indust*. **2002**, *10*, 41–43.
12. A.Kh. Mammadova, *Oil Refin. and Petrochem.*, **2004**, *9*, 40-43.
13. A.Kh. Mammadova., *Oil Refin. and Petrochem.*, **2001**, *1*, 36–38.
14. A.Kh. Mammadova, A.K. Kazimzadeh and E.A. Nagiyeva, *Azerb. Oil Indus.*, **2011**, *8*, 62–65.
15. A.Kh. Mammadova, *Azerb. Oil Indus.*, **2007**, *9*, 57–60.
16. A.K. Kazimzadeh, E.A. Nagiyeva, A.Kh. Mammadova and S.I. Nasirova, *Azerb. Oil Indust.*, **2011**, *1*, 45-50.
17. G.A. Zeynalova, A.Kh. Mammadova, E.A. Nagiyeva, Sh. D.Ibrahimov and B. I.Abdullayev, *USSR Inventor's Certificate*, 163 4663, Nov 11. **1990**.
18. G.A. Zeynalova, A.K. Kazimzadeh, E.A. Nagiyeva, A.Kh. Mammadova and D.T. Agayev, *USSR Inventor's Certificate*, 182 3486, Oct 12. **1992**.
19. L. Savino. Application 2625220, France, **1989**.
20. L.V. Borenko, V.L. Lashkhi, I.G. Fuks and M.A. Lisovskaya, *Chem. and Tech. of Fuels and Oils,* 1**986**, *1*, 44–46.
21. S.V. Monin, A.Ya. Levin, M.S. Khots, E.A. Ivanova and V.N. Volkova, *Oil Ref. and Petrochem.*, **1986**, *10*, 13-15.
22. V.L. Lashkhi, T. Leymeter, G.I. Shor and M.I. Falkovich, *Chem. and Tech. of Fuels and Oils,* **2001**, *5*, 49-51.
23. V.M. Farzaliyev, A.Kh. Mammadova, A.K. Kazimzadeh and E.A. Nagiyeva, Az Pat.İ 20080198. Dec 16 **2008**.
24. A.Kh.Mammadova, *Oil Refin. and Petrochem.*, **2006**, *3*, 42–44.
25. A.K. Kazimzadeh, E.A.Nagiıyeva, A.Kh. Mammadova and R.A. Mammadova, Az Pat. İ 20050136, Oct 14, **2005**.
26. A.K. Kazimzadeh, E.A. Nagiyeva and A.Kh. Mammadova, *Azerb. Oil Indust.*, **2007**, *10*, 47–49.
27. A.Kh. Mammadova, A.K. Kazimzadeh and E.A. Nagiıyeva, *Oil Refin. and Petrochem.*, **2007**, *10*, 32–34.
28. A.K. Kazimzadeh, E.A. Nagiıyeva, A.Kh. Mammadova, R.A. Mammadova and S.İ. Nasirova, Az Pat. İ.20150021. Mar 3. **2015**.
29. V.M. Farzaliyev, A.K. Kazimzadeh, E.A. Nagiyeva, A.Kh. Mammadova and A.A. Gadirov, *Sci. Technol. and High. Educ. Mater. of the V internat. Rese. and prac. conf*. Jun 20. **2014**. *52-56*. Westwood, Canada.
30. Additives to Motor and Transmission Mineral Oils, Masma VNIIPK Neftechim NGO Directory. Kiev, **1985**.
31. V.M. Farzaliyev, A.K. Kazimzadeh, E.A. Nagiyeva, A.Kh. Mammadova and R.A. Mammadova, Az Pat. İ 20080199. Dec 12. **2008**.
32. H.A. Javadova, Kh.G. Afandiyeva, A.Kh. Mammadova, G.G. Yusifzadeh and Z.K. Maharramova, Pat. İ 20150073. Oct 21. **2015**.
33. V.M. Farzaliyev, H.A. Javadova, U.B. Ramazanova, A.Kh. Mammadova, A.A. Huseynova, E.M. Javadova and A.R. Yusifova, Az Pat. İ 20150075. Oct.21. **2015**.