

INFLUENCE OF PROMOTERS ON THE SYNTHESIS OF HIGH-ALKALINE ALKYLPHENOLATE ADDITIVE

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Received 06.05.2024

Accepted 15.07.2024

Abstract: *In world practice, additives based on alkylphenols have become widespread. This distribution of alkylphenol additives is explained by a wide range of performance properties, the relative availability of raw materials and simple production technology compared to the production of other additives. Prior to 1970, alkylphenol additive production in the former Soviet Union accounted for approximately 80% of total lubricating oil additive production. Currently, 70-75% of chemical additives based on alkylphenols are used in industry.*

The growing power of modern gasoline and diesel engines, the tightening of their operation modes impose uplifted demands on the quality of modern motor oils. Improving the quality of motor oils with the help of effective additives is one of the most modern and promising methods used in world practice. To meet the requirements of new engines in high-quality oils, it is necessary to create new modifications of traditional additives (alkylphenolic, sulfonate, dithiophosphate, etc.) of better quality than those currently produced.

The most widely used additives are alkylphenolate additives. Alkylphenolate additives have multifunctional properties and are one of the main components of motor oils.

To obtain motor oils that meet modern requirements, it is necessary to synthesize effective additives.

To ensure long-term and reliable operation of machines, the development and production of efficient motor oils is increasing.

The use of highly alkaline alkylphenolate additives makes it possible to obtain high-quality motor oils of various groups.

Therefore, the synthesis of effective alkylphenol additives, the organization of their production and the creation of high-quality motor oils is one of the pressing problems of petro chemistry.

In this regard, an effective high-alkaline additive AKI-152 was obtained, which is a carbonated calcium salt of the condensation products of dodecylphenol, ammonia, formaldehyde and imidazole. The additive was obtained using various promoters. At the end of the study, the needed promoters to build a more effective additive was revealed.

The AKI-152 additive is not inferior to foreign analogues in terms of functional properties. Therefore, using the AKI-152 additive, M-12B5 motor oil has been developed, which in terms of basic performance properties corresponds to TU Az 3536814-008-2004 for this oil.

Key words: *dodecylphenol, formaldehyde, ammonia, imidazole, additive, property, motor oil.*

DOI: 10.32737/2221-8688-2025-2-178-186

Introduction

In modern times, new types of machines and mechanisms are being created and the technical and economic indicators of existing equipment are being improved, the issue of long-term and reliable operation of vehicles is being resolved, and the available lubricating oils lag behind the needs of the equipment.

Therefore, it is impossible to create a normal operating mode for modern equipment without the use of high-quality lubricating oils. To obtain high-quality lubricating oils, effective additives are required.

In the field of development and application of additives added to lubricating

oils, promising areas are the creation of effective multifunctional additives and updating their range.

One of the directions in the literature for new additives that ensure high performance characteristics of motor oils under conditions of elevated temperatures and loads is the development of multifunctional alkylphenolate additives [1-9]. The interest of chemists in this class of organic compounds is primarily due to the high reactivity of alkylphenols, the availability of starting materials, simple production technology, versatility, as well as the widespread use of these additives in the total volume of commercial additives.

The increased demand for alkylphenol additives not only does not weaken, but even grows from year to year. Highly alkaline alkylphenolate additives are one of the main components of motor oils. The high alkalinity of alkylphenolate additives leads to an increase in their neutralizing properties, which are associated with the suppression of acidic products formed via oil oxidation during their operation [10].

In this regard, research carried out in the direction of the synthesis of highly alkaline alkylphenol additives, the organization of their production and the creation of high-quality motor oils is one of the significant issues of the petrochemical industry.

Experimental part

The goal of the work is the synthesis of a new effective alkylphenolate additive and the development of motor oil based on it.

It is known that a promising direction for the development of modern motor oils is the use of effective alkylphenolate additives [11, 12].

Carbonated alkylphenolates with high alkalinity have become widespread abroad [13-15]. These include additives Paranox-51, Amoco-9230, Amoco-9131, OLOA-218A, ВНИИ НП-714 etc. Highly alkaline alkylphenolate additives neutralize acids formed during engine operation, thereby inhibiting oxidation and improving the anti-oxidation and anti-corrosion properties of the oil.

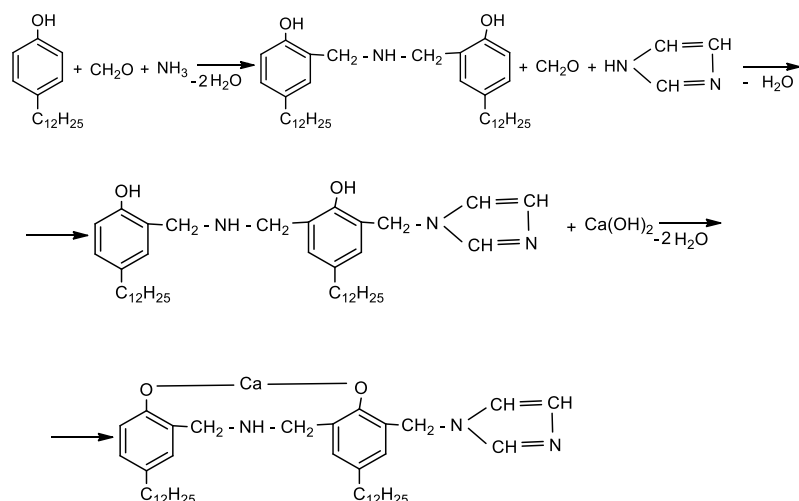
Foreign companies use highly alkaline alkylphenolate additives as the main component

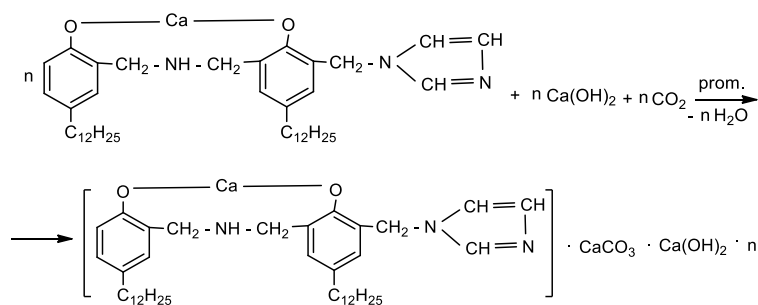
in motor oils. Therefore, a highly alkaline additive AKI-152 was obtained, which is a carbonated calcium salt of the condensation products of dodecylphenol, ammonia, formaldehyde and imidazole.

Dodecylphenol is obtained from alkylation of phenol tetramerpropylene in acidic medium – TC BC 390 401 182 018-2009, formalin GOST 1625-89, ammonia GOST 3760-79, imidazole– TC 6-09-08-1314-78.

High-alkaline alkylphenolate additives are synthesized in the same way as medium-alkaline alkylphenolate additives, only in the neutralization process more than a stoichiometric amount of calcium hydroxide is used; a promoter and carbonation are carried out with carbonation.

Reaction scheme:





When synthesizing the AKI-152 additive, the condensation process is carried out in two stages, first, dodecylphenol with formalin (35% aqueous solution of formaldehyde) and ammonia at 95-98°C, after separation of the aqueous salt, condensation of the resulting product continues with formaldehyde and imidazole at a temperature of 70-75°C, after the reaction is completed, the oil thinner stops the condensation process, then 5g of glycerol (promoter) is added and the neutralization process begins (40% for alkylphenol) with calcium hydroxide at 80-85°C, carbon dioxide is supplied for 4.5 hours, then drying at a temperature of 115-120°C, jointing and isolation of the target product.

The structure of the AKI-152 additive was proven by IR spectroscopy, which was carried out on an American-made «Nicolet Is-10» Fourier spectrometer in the region of 4000-400 cm⁻¹.

The spectra of the condensed product (Fig. 1), salts of the condensed product before carbonation (Fig. 2) and after carbonation are presented (Fig. 3).

In the IR spectrum of the condensed product additives AKI-152 a wide absorption band appears in the form of a dimer of stretching vibrations of the OH group in the region $\nu_{\text{OH}} = 3334.89 \text{ cm}^{-1}$, in the spatially hindered position of the OH bond, a thin absorption band $\nu_{\text{OH}} = 3582.80 \text{ cm}^{-1}$ and stretching vibrations of NC, C=N, C=C bonds are respectively equal to $\nu_{\text{NC}} = 1182.77 \text{ cm}^{-1}$, $\nu_{\text{C=C}} = 1611.68 \text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1652.18 \text{ cm}^{-1}$ (Fig. 1).

When a salt is formed, the broad absorption band of stretching vibrations of the OH group at $\nu_{\text{OH}} = 3334.89 \text{ cm}^{-1}$ disappears. The remaining bond stretching vibrations remain in a slightly modified form: $\nu_{\text{NC}} = 1190.28 \text{ cm}^{-1}$, $\nu_{\text{C=C}} = 1605.65 \text{ cm}^{-1}$, $\nu_{\text{C=N}} = 1632.73 \text{ cm}^{-1}$ (Fig. 2).

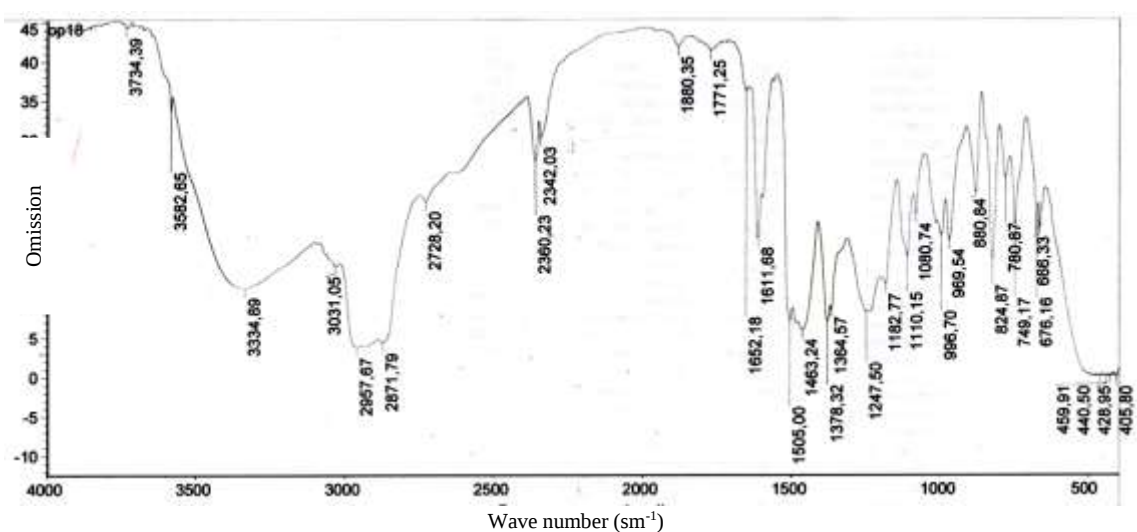


Fig. 1. IR spectral of condensation product of dodecylphenol, formaldehyde, ammonia and imidazole

After carbonation, an absorption band $\nu_{\text{OH}}=3176.19 \text{ cm}^{-1}$ appears, which characterizes the hydroxyl group in $\text{Ca}(\text{OH})_2$, $\nu_{\text{CO}_3}=1601.57$

cm^{-1} characterizes CO_3 in CaCO_3 , and the remaining absorption bands remain with minor changes (Fig. 3).

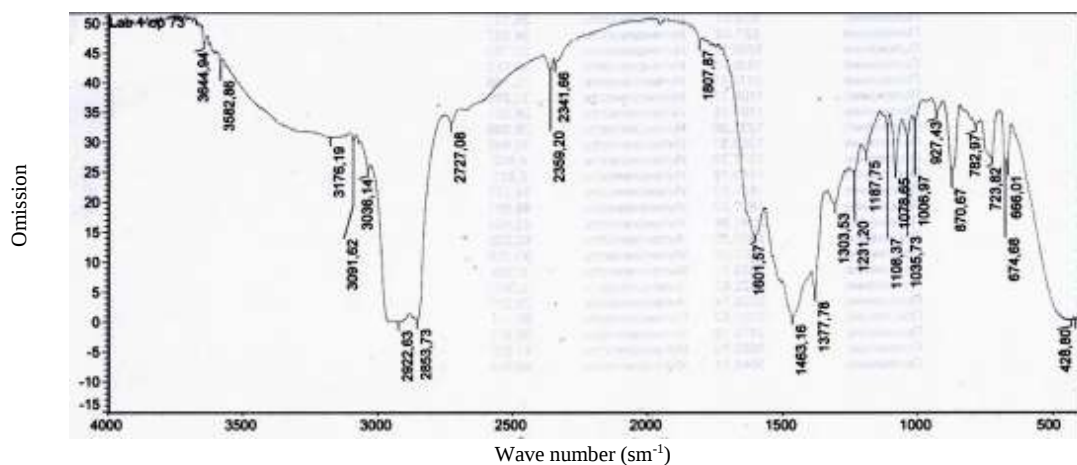


Fig. 2. IR spectral of calcium salt of condensation product of dodecylphenol formaldehyde, ammonia and imidazole

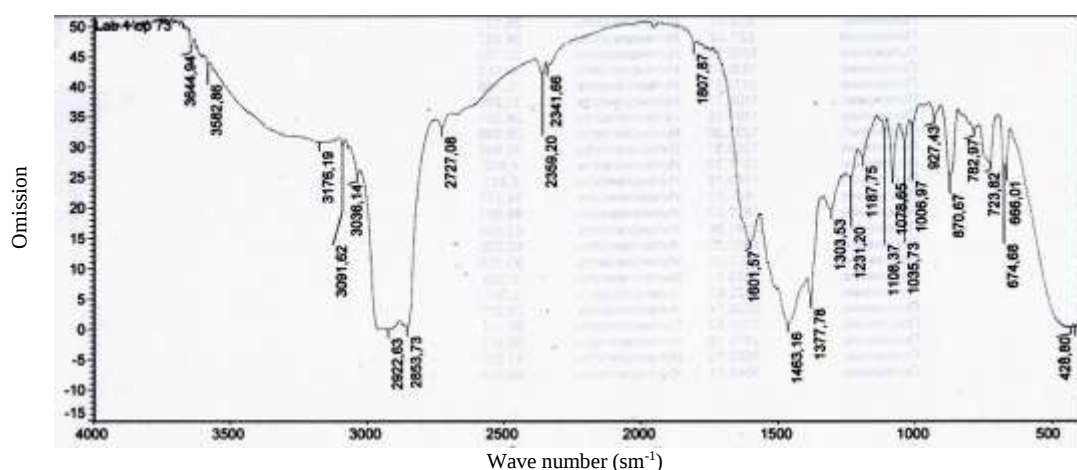


Fig. 3. IR spectral of carbonated calcium salt of the condensation product of dodecylphenol, formaldehyde, ammonia and imidazole

One of the main stages in the synthesis of high-alkaline additives is the carbonation process, since at this stage the colloidal stability of the additives is formed, ensuring their high alkalinity, good detergent and other functional properties.

The colloidal stability of the additive is affected by the viscosity of the medium, temperature, promoters etc.

Using promoters, highly alkaline alkylphenolate additives are obtained. Promoters are added either at the neutralization stage or at the carbonation stage.

Various types of promoters are used in the production of highly alkaline additives: monohydric and polyhydric alcohols, amino alcohols, acids, amino acids, amines, peroxides [16-25] and others. For a reasonable selection of promoters, it is advisable to study their effect on the properties of a high-alkaline alkylphenolate additive.

Studies have been carried out to compare the properties of additives obtained under the same conditions using different promoters and to evaluate the technological advantages of a particular method.

Results and discussion

This article presents the results of studies of the influence of promoters on the physicochemical and functional properties of the AKI-152 additive. For the synthesis of the additive, acetic acid, polyhydric alcohols - glycerol, ethylene glycol, alkanolamine - diethanolamine.

Typically, promoters are introduced into the reaction at both the neutralization and carbonation stages. We introduce the promoter into the reaction during neutralization. Physicochemical and functional properties of additives were determined by standard methods:

- anti-corrosion properties according to GOST 9490-75;
- stability according to the induction method of sedimentation for 30 hours according to GOST 11063-2020;
- detergent properties according to the PZW method GOST 5726-2013.

It is called by the first letters of the surnames of the discoverers of the PZW method.

Papok, Zarubina, Whipper.

The lab research analysis and results are shown in Table 1.

Table 1. Physico-chemical and functional properties of AKI-152 additive

Promoters	Base number, mgKOH/g	Kinematic viscosity, at 100°C, mm ² /s	Concentration of additives in oil, %	M-8 oil with additive		
				Corrosivity (in lead plates), g/m ²	Stability by induction period of sedimentation (ISP), 30h sediment, %	Cleaning properties (according to PZW), point
Acetic acid	140.1	54.6	3	1.6	0.65	0.5
			5	1.0	0.72	0.5
1%	146.6	58.8	3	1.5	0.70	0.5
			5	1.0	0.75	0.5
Ethylene glycol	143.8	61.7	3	1.0	0.40	0.5
			5	0.95	0.45	0.5
3%	155.4	64.4	3	0.82	0.28	0.5
			5	0.90	0.25	0-0.5
Glycerol	145.2	67.4	3	1.1	0.35	0.5
			5	0.85	0.40	0.5
3%	157.7	70.3	3	0.75	0.48	0.5
			5	0.80	0.45	0.5
Diethanolamie	160.4	74.1	3	2.1	1.8	1.0
			5	1.9	2.5	0.5-1.0
3%	158.6	81.3	3	1.8	2.1	1.0
			5	1.2	2.8	0.5-1.0

As can be seen from the table data, the best results are achieved by additives obtained with the promoters ethylene glycol and glycerin.

When diethanolamine is used as a promoter, the additive acquires an alkalinity slightly higher (158.0-160.4 mgKOH/g) than that of additives obtained with other promoters, but at the same time its antioxidant and detergent properties deteriorate, which is apparently due to the instability colloidal structure of the additive.

At the carbonation stage, a stable colloidal

micellar structure should be formed. The carbonation process determines the colloidal stability and, accordingly, the effectiveness of additives. Colloidal stability is affected by the viscosity of the medium, temperature, promoters, etc.

At the carbonation stage, a stable colloidal micellar structure should be formed. It is known in the literature that highly alkaline sulfonates, alkyl salicylates and alkyl phenolates have the same micellar colloidal structure [26]. The micelle core consists of calcium carbonate and

an adsorption-solvation shell, in this case, calcium alkylphenolate (Fig. 4).

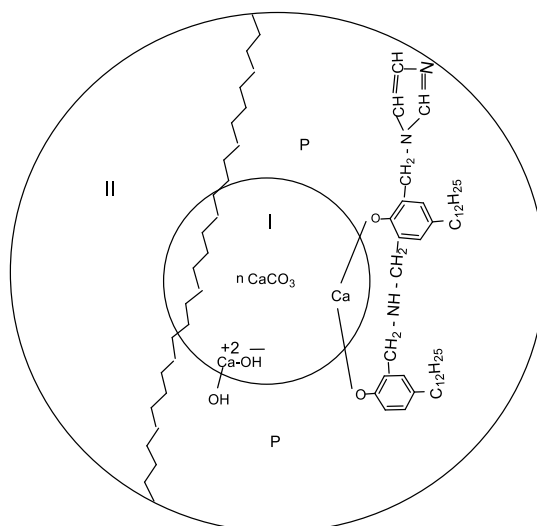


Fig. 4. Proposed scheme of a colloidal micelle AKI-152 additive structures
I- micelle core, II- adsorption - solvation shell, P - molecules of diluent oil

Additives with colloidal stability determine the main degree of quality of petroleum products. During long-term storage of additives in solution, if no precipitate forms, this indicates their colloidal stability.

Table 2 shows the comparative physicochemical and functional properties of

the additive AKI-152 and foreign analogues OLOA-218A and ВНИИ НП-714 (carbonated calcium sulfidealkylphenolates). As follows from the data in Table 2, the AKI-152 additive is superior in anti-corrosion properties to its analogues, and is on par with them in its anti-oxidation and detergent properties.

Table 2. Physicochemical and functional properties alkylphenolate additives

Samples additives with hetero-atoms	Base number, mgKOH/g	Sulfate-ash content, %	Oil M-8 with 5% additive		
			Corrosivity (in lead plates), g/m ²	Stability by induction period of sedimentation (ISP), 30h sediment, %	Cleaning properties (according to PZW), point
AKI-152	157.7	18.8	0.80	0.45	0.5
AKI-152	155.4	17.5	0.90	0.25	0.5
ВНИИ НП-714	155.0	20.5	7.5	0.47	0.5
ВНИИ НП-714	143.0	17.2	6.4	0.41	0.5
ОЛОА-218A	147.0	17.6	9.8	0.45	0.5

In Azerbaijan, the base oils produced are mainly with a low viscosity index and low pour point, so the development of motor oils is associated with some difficulties, the need to use additives that increase the viscosity index, reduce the pour point of oils and take into account the synergy of the additives used. Taking these facts into account, M-12BБ motor oil was developed based on the AKI-152

- ✓ AKI-152 – multifunctional alkylphenolate additive,
- ✓ C-150 – detergent-dispersant additive,

additive and industrial additives.

The developed motor oil consists of the following additive composition: Viscoplex 2-670+AKI-152+ДФ-11+C-150+C-A+Viscoplex 5-309+ПМС-200А (Table 3). Baku oil M-10 was used as base oil. Viscoplex 2-670 – is a polymethacrylate type additive that increases the viscosity index of the oil,

- ✓ ДФ-11 – antioxidant dithiophosphate additive,
- ✓ C-5A – dispersing succinimide additive,
- ✓ Viscoplex 5-309 is a polymethacrylate type additive that lowers the pour point,
- ✓ ПМС-200А – polymethylsiloxane, anti-foam additive.

Table 3 demonstrates the functional properties of the experimental motor oil M-12BБ and the foreign analogue from «Shell». Evaluation of the functional properties of the experimental oil using standard methods showed that the developed M-12BБ motor oil complies with the specifications for this oil.

As can be seen from the data in Table 3, assessment of the functional properties of the experimental oil using standard methods showed that the developed M-12BБ motor oil meets the requirements of the technical specifications for this oil and is at the level of foreign oil from «Shell».

Table 3. Physicochemical and functional properties motor oils M-12BБ

Indicators	TY 3536814- 008-2004	M-12BБ Commercial oil	Experienced oil	Shell Rotella X	Test methods	
					GOST	ASTM
Kinematic viscosity, at 100°C, mm ² /s	11.5-13.0	12.0	12.8	10.8	33	D 445
Viscosity index, no less	77	80	90	102	25371	D 2270
Base number, mgKOH/g, no less	5.0	5.5	7.8	8.0	11362	D 2896
Sulfate ash content, %, no more	1.3	1.3	1/28	1.3	12417	D 874
Flash point in an open crucible, °C, not lower	205	205	215	218	4333	D 92
Pour point, °C, no more	Minus 15	Minus 15	Minus 15	Minus 15	20287	D 97
Induction period sedimentation (ISP), 40h	Withst- ands	Withst-ands	Withst-ands	Withst- ands	11063	–
Corrosion on lead plates, g/m ² , no more	10	6.0	Abcent	Abcent	20502	D 665 opt 2, met. A
Cleaning properties (according to PZW), point, no more	0.5	0.5	0/5	0.5	5726	D 892

Conclusions

It must be noted that as a result of new and more effective additive development for motor oils, a high-alkaline alkylphenolate additive – “AKI-152” with high performance properties was obtained.

The use of the AKI-152 additive, in various combinations with sulfonate and other additives, will make it possible to create modern motor oils of various series at the level of foreign analogues.

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