Synthesis and Study of Modified Alkylphenolate Additives for Motor Oils

Nagiyeva, Elmira; Farzaliyev, Vagif; Kazimzadeh, Ali; Ramazanova, Yulduz; Mammadyarova, Khadija; Mammadova, Rahila; Sujayev, Afsun [*+]

Institute of Chemistry of Additives, Azerbaijan National Academy of Sciences, Baku, AZERBAIJAN

ABSTRACT: *The article presents the results of research on the synthesis of new medium alkaline AKI-31, AKI-57, and high alkaline additives AKI-124 and AKI-134. Additives AKI-31 and AKI-57 are calcium salts of condensation products of dodecylphenol, formaldehyde, and amino acetic (AKI-31) or p-aminobenzoic (AKI-57) acid. Highly alkaline additives AKI-124 and AKI-134 are carbonated calcium salts of condensation products of dodecylphenol, formaldehyde, and amino acetic acid (AKI-124) or p-aminobenzoic acid (AKI-134). The high-performance properties of the additives have been confirmed by standard research methods. Studies have shown that the additives have high antioxidant, anticorrosive, and detergent properties. Highly alkaline additives AKI-124 and AKI-134 were studied by thermal analysis methods. It is shown that the additives are highly resistant to temperature effects. By using highly alkaline additives, M-10G2 motor oils have been developed, which in terms of basic performance indicators correspond to GOST 8581-92 and are on a par with the foreign analog of Shell.*

KEYWORDS: *Dodecylphenol; Formaldehyde; Aminoacetic acid; P-aminobenzoic acid; Additive; Corrosion; Stability; Thermal analysis; Motor oils.*

INTRODUCTION

In the composition of modern engine oils based on minerals, detergent-dispersant additives play a significant role.

Detergent-dispersant additives are designed to reduce deposits on parts of internal combustion engines.

This group of additives includes metal-containing compounds - sulfonates, phenates, salicylates (mainly calcium, magnesium), as well as ashless compounds - succinimide derivatives, various copolymers et al. [1-4].

The creation of motor oils for modern technology requires the development of effective additives with various functional effects.

A significant part of detergent-dispersant additives widely used in motor oils are alkylphenolic metal additives.

Alkylphenolate additives have a wide range of performance properties, relatively simple production technologies and the availability of raw materials. In addition, they are used as the main component in the creation of engine oils of various groups [5-9].

Before 1990, barium and calcium salts of alkylphenolate additives for motor oils (BFK, AKI-101, CIATIM-339, VNIINP-370, AKI-109, etc.) with an alkalinity level of 35-60 mgKOH/g [10] were produced. At this stage they played a large role in the development of motor oils.

However, at present, the low level of performance properties of these additives does not allow their use in the

* *To whom correspondence should be addressed.*
+E-mail address: s.afsun@mail.ru
1021-9986/2022/12/4098-4103 6/$/5.06

production of modern motor oils that meet the requirements of the motor industry.

Detergent-dispersing action is the most important functional nym property of additives to motor oils. The effectiveness of detergent-dispersant additives is primarily related to their ability to maintain the aggregate stability of colloidal dispersions of oil aging products.

Improving the quality of engine oils using effective detergent and dispersant additives is one of the most modern and promising methods used in world practice.

The effectiveness of detergent-dispersant additives is associated with the micellar nature of their solutions in oil, which are capable of including various oil-insoluble substances in their structure, thereby converting them into a colloidal solution. An important characteristic of detergent-dispersant additives can be the temperature at which micelles break down. Alkyl salicylates have the highest micelle destruction temperature (~ 220˚C) sulfonates (180-190˚C), succinimides (130-160˚C) [11]. These indicators to a certain extent determine the temperature range of the use of additives in the composition of lubricating compositions.

Taking this factor into account, the creation of salicylate additives that combine high efficiency with thermal stability is becoming increasingly important. Additives of this type play an important role in the development of oils of various series for modern heat-stressed engines.

From year to year, engine designs are being improved, new types of machines with increased engine power and service life are created. This, in turn, is associated with the inevitability of improving the quality of engine oils.

A rational way to improve the quality of motor oils is the use of additives for various purposes, among which salicylate-type additives play an important role.

However, in the industry, alkyl salicylate additives are obtained using a multistage and complex technology, which makes it difficult to create a rational technology for their production [12].

In this regard, the synthesis and research of new additives containing a carboxylate group, which are obtained by simple technology and have high-performance properties, have been carried out.

EXPERIMENTAL SECTION

General chemistry

Additives are obtained by sequential condensation first of dodecylphenol with formalin (35% aqueous solution of formaldehyde) and ammonia at a temperature of 95-98°C, after completion of the reaction, the aqueous layer is separated, then the condensation of formalin with aminoacetic (or p-aminobenzoic) acid continues at 80-90°C in the presence of a calcium hydroxide catalyst - 1.5%, an aqueous layer is separated into alkyl phenol. Then neutralization with calcium hydroxide is carried out, drying and the target product is separated by centrifugation [13].

The optimal conditions for obtaining additives have been found:

dodecylphenol: formaldehyde: ammonia: aminoacetic (*p*-aminobenzoic) acid: $Ca(OH)_2$ - 1:0.4:0.3:0.08(0.1):0.2

The resulting additives are viscous liquids with a base number of 94-100 mgKOH / g, sulphated ash content of 11.0-13.5%. nitrogen 2.0-2.2%.

Material and methods

The structure of the synthesized additives was confirmed by IR spectroscopy.

At present, the synthesis of multifunctional additives that combine high-efficiency rates with high thermal stability is gaining great importance.

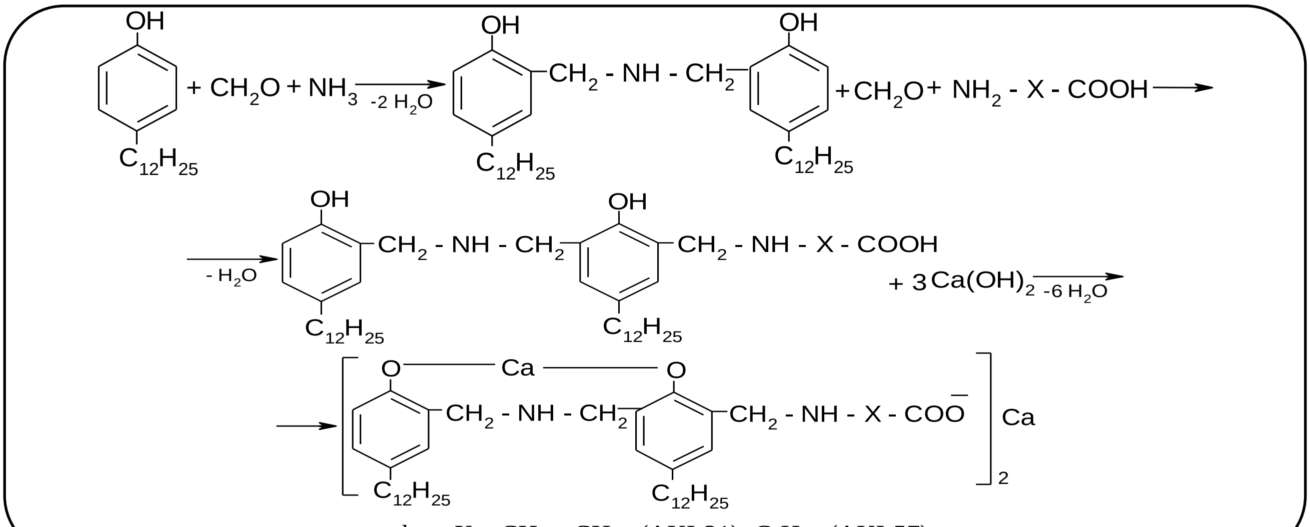
Therefore, it was interesting to study the thermal stability of the synthesized additives AKI-124 and AKI-134.

The thermal stability of the additives AKI-124 and AKI-134 have been investigated.

Thermoanalytical studies were carried out on an OD-102T derivatograph (MOM, Hungary) in a dynamic heating mode at a rate of 10˚C/min in air. Calcined aluminum oxide served as a standard; the weighed portions of the samples were 0.1 g.

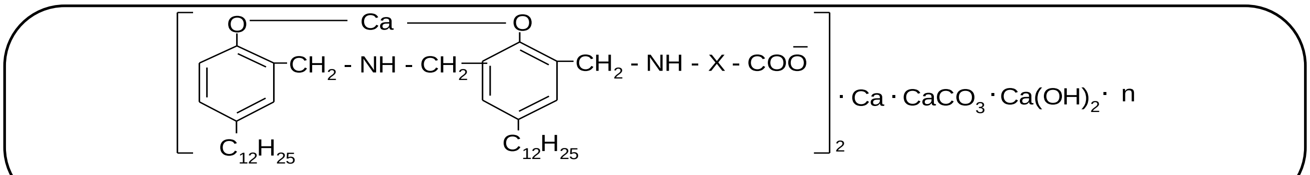
The functional properties of the additives were investigated by standard methods: anticorrosive properties according to GOST 20502-75, resistance to oxidation according to the induction period of sedimentation (IPO) for 30 hours according to GOST 11063-77, washing properties according to ELV 5226-2013.

The criteria for evaluating the thermal-oxidative stability of the samples were taken to be temperatures corresponding to equal shares of their mass loss with increasing temperature, determined from thermogravimetric (TG) curves, for example, $T_{10\%}$, $T_{50\%}$; temperatures of the end of the first (beginning of the second) stage of their Thermo oxidative destruction, as well as the temperature of the onset of the exothermic effect of Thermos oxidative



where X – CH_2 – CH_2– (AKI-31); C_6H_4– (AKI-57)

Scheme 1: Synthesis of new additives (AKI-31 and AKI-57)



where X – CH_2 – CH_2– (AKI-124); –C_6H_4– (AKI-134)

Scheme 2: Synthesis of AKI-124 and AKI-134.

decomposition of samples, recorded by Differential Thermal Analysis (DTA) curves.

The square-law error of the average result of determining the desired parameters did not exceed 0.4; the relative error of the experiment averaged no more than 1.2%.

RESULTS AND DISCUSSIONS

This work presents the results of synthesis and research on the preparation of new detergent-dispersing alkyl phenolate additives containing phenolate and carboxylate groups, like alkyl salicylate additives, but unlike them, they also contain a nitrogen atom and can be obtained using simple technology.

Medium alkaline additives are the calcium salt of the condensation product of dodecylphenol with formaldehyde, ammonia and aminoacetic acid (AKI-31) or *p*-aminobenzoic acid (AKI-57).

The formation of other condensation products and their salts is also possible.

One of the methods for improving the functional properties of additives is also increasing their base number [14, 15]. Highly alkaline additives have high neutralizing properties and neutralize acids formed during oil oxidation, increasing the antioxidant and anticorrosive properties of the oil.

In recent years, highly alkaline alkyl phenolate additives have been used as the main component of motor oils [16-20].

In this regard, we have obtained highly alkaline versions of the AKI-31 and AKI-57 additives – the AKI-124 and AKI-134 additives. When obtaining additives, the optimal conditions for obtaining medium alkaline additives were used, only in contrast to them, during carbonation, a threefold excess of calcium hydroxide from the stoichiometric one, a promoter of ethylene glycol (5%) is taken and carbon dioxide is supplied in an amount of 14 g.

The resulting additives are viscous liquids with an alkaline numeric of 145-155 mgKOH/g, sulfate ash content 16.0-17.0%, and calcium content 4.5-5.5%.

In the IR spectrum, an intense broad band of the OH group of -3400cm^{-1} and an intense band of the COOH group of 1700-1760 cm^{-1} of condensed products disappear due to the formation of a salt, asymmetric, and symmetric stretching vibrations of the ϑ^{ac}-1620cm^{-1} and $\vartheta^{sim.}$-1364.7cm^{-1} ions appear.

Table 1: Physicochemical and functional properties of additives in comparison with analogues

Additives	Physicochemical properties of the additive			Oil with 5% additive		
	Alkaline numeric, mgKOH/g	Sulphated ash content, %	Kinematic viscosity mm^2/s	Corrosion on lead plates, g/m^2	Induction stability period of sedimentation (IPO, 30h) sediment, %	Detergent properties according to ELV, score
AKI-31	96.5	12.5	83.4	1.5	0.15	0.5
AKI-57	95.4	11.8	85.4	1.2	0.3	0.5
ASK	56.4	7.5	–	35.1	0.8	0.5
ÇIATIM-339*	42.0	10.3	–	31.4	3.5	0.5
AKI-101	64.8	12.0	56.8	15.0	3.2	0.5

* 10% concentration in oil

Table 2: Physicochemical and functional properties of highly alkaline alkyl phenolate additives

Additives	Physicochemical properties of the additive			Oil with 5% additive		
	Alkaline numeric, mgKOH/g	Sulphated ash content, %	Kinematic viscosity mm^2/s	Corrosion on lead plates, g/m^2	Induction stability period of sedimentation (IPO, 30h) sediment, %	Detergent properties according to ELV, score
AKI-124	148.6	16.4	67.5	0.5	0.1	0.5
AKI-134	152.2	16.7	75.2	0.8	0.25	0.5
VNIINP-714	143.0	17.2	–	6.2	0.42	0.5
OLOA-218A	147.0	17.6	–	9.6	0.46	0.5
MASK	140.0	16.8	–	4.3	0.41	0.5

In condensed products, the absorption bands of NH groups overlapped by the absorption bands of OH groups, in the additives, stretching vibrations of NH groups are observed in the regions of 3368.7 cm^{-1} and 3188.5 cm^{-1}.

Table 1 shows the physicochemical and functional properties of the additives, as well as comparative results of studies of industrial additives ASA (calcium alkyl salicylate), ÇIATIM-339 (barium disulfide alkyl phenolate), AKI-101-barium alkyl phenolate.

As studies have shown, the synthesized additives are superior to the additives of the product range in terms of functional properties (Table 1).

Thus, oil M-8 with synthesized additives has a corrosion of 1.2-1.5 g/m^2, a sludge of 0.15-0.3%, and with industrial additives, corrosion is 18.0, 21.4, and 45.1 g/m^2, and sludge is 4.2, 3.4, 1.1%, respectively.

The functional properties of the AKI-124 and AKI-134 additives were also investigated by standard methods (Table 2).

From the data table. 2, it can be seen that highly alkaline additives AKI-124 and AKI-134 are superior in anti-corrosive properties to highly alkaline analogs - commercial additives, so the corrosion and sediment of the synthesized additives are 0.5 and 0.8 g / m2, and the sediment is 0.1 and 0.25%, respectively, against 6.2, 9.6 and 4.3 g / m^2 and 0.42, 0.46 and 0.41% for analogs, and for antioxidant and anticorrosive medium alkaline additives AKI-31 and AKI-57.

The studied additives underwent thermal oxidative degradation mainly in three stages. Stage I of decomposition of additives AKI-124 and AKI-134 is fixed on their TG curves in the temperature range of about 260-360°C, the weight loss at this stage was 12% for AKI-124 and 40% of the initial sample for AKI-124. It is largely due to the thermal destruction of the oil thinner added to the additives during their synthesis. So, possibly, the remainder of the alkylphenol, which did not enter into the condensation reaction, and the destruction of weak links in the chains of its radical.

With a further increase in temperature, the curves of thermal analysis record the II stage of decomposition, which characterizes the thermochemical transformations of, probably, directly of the additives. The next stage of decomposition at temperatures above 445°C on average is accompanied by oxidation (charring) of the destruction products.

Table 3 shows the effect of additives on the thermal-oxidative stability of M-8 oil.

According to table 3, the temperature of the beginning of the second stage of thermochemical transformations, that is, the thermal stability of the synthesized additives is about 360°C.

Table 3: Influence of additives on the thermal-oxidative stability of M-8 oil

Sample	Temperature of exothermic effect of thermal oxidative decomposition of M-8 oil, °C		$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$, °C
	start of effect	maximum effect			
M-8	300	337	305	330	380
M-8+5% AKI-124	311	350	311	334	392
M-8+5% AKI-134	317	360	321	345	402

Table 4: Physicochemical and functional properties of motor oils M-10G2

Indicators	GOST-8581-92 (norm)	Experienced oil with additive AKI-124	Experienced oil with additive AKI-134	Commodity oil M-G_2	Shell Rimula C30	Test methods	
						GOST	ASTM
Kinematic viscosity, at 100°C, mm^2/s	11.0±0.5	11.11	11.25	11.5	10.8	33	D 445
Viscosity index, not less	85	90	90	90	102	25371	D 2270
Alkaline numeric, mgKOH/g, not less	6.0	8.1	8.2	7.2	9.4	11362	D 2896
Sulphated ash content, %, not less	1.65	1.3	1.28	1.29	1.3	12417	D 874
Flash point in an open crucible, °C, not less	205	210	210	210	202	4333	D 92
Pour point, °C, not lower	minus 15	minus 15	minus 15	minus 15	minus 15	20287	D 97
Induction period sedimentation (IPO), withstands, h	40	40	40	40	40	11063	–
Corrosion on lead plates, g/m^2, no more	20	absent	Absent	5.2	absent	20502	D 665 option 2, method A
Detergent properties (by ELV), point, no more	1.0	0.5	0.5	0.5	05	5726	D 892

The AKI-134 additive has a slightly higher thermal stability, the presence of a benzyl radical increases its thermal stability in comparison with the AKI-124 additive by 10°C.

The studies carried out to determine the thermal stability of the AKI-124 and AKI-134 alkyl phenolate additives showed that the additives have sufficiently high thermal stability, reaching a temperature of about 360°C.

To create high-quality engine oils that meet the standards of modern and promising technology, additives that are more effective than commercial samples are required.

Motor oils M-10G2 with synthesized additives AKI-124 and AKI-134 have been developed.

The development of motor oils in Azerbaijan is associated with certain difficulties. This is primarily due to the low viscosity-temperature properties of base oils. In addition, one of the main components of commercial oils is the additive AKI-101 (barium alkyl phenolate), which has a high ash content, low alkalinity, and exhibits weak anticorrosive properties.

When creating a composition of motor oil, the main attention was paid to identifying the synergistic effect between the synthesized and commercial additives, reducing the ash content and increasing the oil viscosity index.

Experimental alkylphenolate additives AKI-124 or AKI-134 were investigated in the composition instead of additives AKI-101, as well as industrial additives Viscoplex 2-670, DF-11, S-150, S-5A, Viscoplex-5-309, PMS-200A, as the base oil M-8 oil was used.

Evaluation of the functional properties of the test oils by using standard methods showed that they correspond to GOST 8581-92 in terms of their main performance indicators and are on a par with the foreign analogue of Shell, and in terms of antioxidant and anticorrosive properties they are superior to commercial oil (Table 4).

CONCLUSIONS

Thus, to obtain modern engine oils, it is necessary to obtain effective additives. For this purpose, new medium alkaline AKI-31, AKI-57, and high alkaline additives AKI-124 and AKI-134 have been synthesized. Medium alkaline additives surpass analogs of ASK, ÇIATIM-339, AKI-101 in performance properties, high alkaline additives surpass medium alkaline additives in performance properties, and foreign analogues VNIINP-714 and OLOA-218A in terms of anticorrosive properties. Studies have shown that AKI-124 and AKI-

134 additives have high anticorrosive, antioxidant, and detergent properties, high thermal stability, and, in combination with other commercial additives, make it possible to create modern motor oils at the level of foreign analogues.

Received: Oct. 18, 2021 ; Accepted: Jan. 10, 2022

References

[1] Guliyev A., "Chemistry and Technology of Oil and Fuel Additives", Publishing House Chemistry, Leningrad/Russian (1985).

[2] Vipper A., Antioxidant Properties of Engine Oil Detergent Additives, *Lubrication Science*, **9(1):** 61-70 (1996).

[3] Nagieva E., Mammadyarova K.h., Abdullayev B., Abdullayev B., Mamedova R., Aminocontaining Alkylphenolate Additives, *Oil Refining and Petrochemistry*, **1:** 39-40 (2018).

[4] Kazim-zade A., Nagieva E., Mammadyarova Kh., Gadirov A., Mamedova R., Abdullaev B., Mirzoeva M., Multifunctional Alkylphenolate Additives to Motor Oils, *World of Oil Products*, **6:** 52-55 (2020).

[5] Kirichenko G., Glazunova V., Desyatkin A., Ibragimov A., Dzhamilov U., Synthesis of New Polyfunctional Additives for Lubricating Oils, *Journal of Applied Chemistry*, **1:** 94-98 (2009).

[6] Moiseeva L., Multifunctional Additives-Alkylphenols: Improvement of Production Methods, *Mechanical Engineering Technology*, **10:** 37-47 (2012).

[7] Mamedova A., Farzaliev V., Kazim-zade A., New Sulfur-, Nitrogen and Boroncontaining Multifunctional Alkylphenolate Additives For Motor Oils, *Petrochemistry*, **57(8):** 718-721 (2017).

[8] Kazimzade A., Nagiyeva E., Farzaliyev V., Gadirov A., Aliyeva M., Abdullayev B., Mammadova R., Nasirova S., Mammadyarova X., Dadashova T., Method of Obtaining Multifunctional Alkylphenolate Additive for Motor Oils, *Az. Patent I 2017 0047* (2017).

[9] Javadova H., Nagiyeva E., Efendiyeva H., Efendiyeva Kh., Abdullayev B., Ismayilov I., Maharramova Z., Yusifzadeh G., Engine Oil for Ships, Locomotives and Stationary Diesels, *Az. Patent I 2016 0024* (2016).

[10] Selezneva I., Levin A., Monin S., Detergent-Dispersing Additives for Motor Oils, *Chemistry and Technology of Fuels and Oils*, **6:** 39-43 (1999).

[11] Bratkov A., "Theoretical Foundations of Chemotology", Chemistry, Moscow/Russian, (1985).

[12] Gordash Yu., Alkylsalicylate Additives to Motor Oils, *Oil Refining and Petrochemistry*, **7:** 43-45 (1992).

[13] Kazimzade A., Nagiyeva E., Farzaliyev V., Gadirov A., Mammadova R., Nasirova S., Mammadyarova X., Method of Obtaining Carboxylate-Containing Multifunctional Additive for Motor Oils, *Az. Patent I 2019 0070* (2019).

[14] Lashkhi V., Leimeter T., Shor G., Falkovich M., Base Number as an Indicator of Compatibility of Additives to Motor Oils, *Chemistry and Technology of Fuels and Oils*, **5:** 49-51 (2001).

[15] Bratko D., Lashkhi V., Shor T., New Super-Alkaline Alkylphenol Additive for Motor Oils, *Journal of Oil and Gas Technology*, **3:** 31-32 (2017).

[16] Selezneva I., Levin A., Trofimova G., Ivanova O., Budanovskaya G., Detergent-Dispersing Alkylphenolate Additive for Motor Oils, *Chemistry and Technology of Fuels and Oils*, **4:** 10-12 (2009).

[17] Kazim-zade A., Nagieva E., Farzaliyev V., Modification of a Multifunctional Alkylphenolate Additive, *Oil Refining and Petrochemistry*, **12:** 44-46 (2012).

[18] Mamedova A., Kazim-zade A., Javadova E., Nasirova S., Heteroatom-Containing Multifunctional Additives based on Dodecylphenol, *Oil Refining and Petrochemistry*, **7:** 33-37 (2018).

[19] Nagiyeva E., Gadirov A., Kazimzade A., Mammadyarova K., Mammadova R., Nasirova S., Multifunctional Alkylphenolate Additive for Motor Oils, *Azerbaijan Oil Industry*, **11:** 51-54 (2020).

[20] Kazimzade A., Nagiyeva E., Gadirov A., Farzaliyev V., Gadirov A., Farzaliyev V., Aliyeva M., Abdullayev B., Mammadyarova Kh., Mammadova R., Nasirova S., Dadashova T., Method of Obtaining Multifunctional Additive to Motor Oils, *Az. Patent I 2021 0074* (2021).