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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS AND INVESTIGATION OF SULFUR AND NITROGEN CONTAINING MULTIFUNCTIONAL ALKYLPHENOLATE ADDITIVES FOR MOTOR OILS

Speciality: **2314.01− Petrochemistry**

Field of science: **Technique**

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INTRODUCTION

The topicality of the subject. As engine construction progresses the corrosion prevention of details, mainly, normal operation of engines at large temperature intervals and other maintenance problems arise.

These problems impose new requirements on the properties of motor oils - corrosion, anti-oxidation, thermal stability, detergents.

The requirements for modern and promising engine oils can be met by developing a new type of quality, a variety of functional additives.

One of the main components of motor oils are metal-detergent-dispersing additives. These additives are alkylphenolate, alkylsisylate and sulfonate additives. In the world, alkylphenolate based additives are more preferred. This is due to their simple acquisition technology, easy access to raw materials and multifunctional properties.

It is possible to increase the functional properties of alkylphenolate additives by adding different heteroatoms and functional groups. Wide practical possibilities of alkylphenol − based products allow obtaining various modifications of alkylphenolate additives and expanding application areas by increasing their assortment.

The demand for sulfuric and nitrogen-containing organic compounds, especially their multifunctional agents, used in various sectors of the economy has increased in recent years.

Given these factors, one of the urgent problems of oil chemistry is to focus on the targeted synthesis of new, sulfur- and nitrogen-fixing alkylphenolate additives, which are superior to industrial designs for their operational properties.

The study was carried out on the research plan 0101Az 00107 at the Institute of Chemistry of Additives after academician A.M. Guliyev of ANAS. Part of the work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan (Grant No. EIF / GAM -4- BGM - GIN - 2017-3 (29) - 19/05/04).

The object and subject of research. Synthesis and research of new multifunctional alkylphenolate additives for motor oils. Creation of high-quality detergent, corrosion and anti-oxidation additives for motor oils.

The purpose of the work. Synthesis of modifications of alkylphenolate additives containing a variety of functional sulfur, nitrogen atoms and various functional groups, studying the dependence between their chemical composition and properties, the development of modern engine oils with the use of synthesized additives.

The following studies are planned to achieve this goal:

– the harmless method of sulfuric alkylphenolate additives;

– Acquisition of aminometry of alkylphenol with various amines and amino acids, calcium alkylphenolate additives from thiomethylation reaction with dodesylmerkaptan and processing with calcium hydroxide;

– obtaining calcium alkylphenolate additives from amino acids di (hydroxyalkylbenzyl) amino acids, thiometric reactions with dodecylmercaptan and thioglycolic acid and calcium hydroxide treatment;

– acquisition of alkylphenolate additives of various types of alkylsalicylate type;

– study of the physical and chemical properties of the synthesized compounds, the determination of the element composition and the chemical structure through IR-spectroscopy;

– research of the dependence between the composition and properties of the synthesized substances;

– research of the corrosion, oxidation and detergent properties of the synthesized compounds;

– development of new modern engine oils with the use of synthesized compounds.

Research methods. During the work, chemical (GOST and ASTM quality indicators), IR-spectr and element analysis methods were used.

Basic provisions for defense. Study of functional properties of new and intermediate alkylphenolate additives containing various S,

N and carboxylate based on thiometry, aminometry and formaldehyde condensation reactions. Creation of motor oils M-8V, M-10G_2, M-12V_2, M-14G_2 using them and industrial additives.

Scientific novelty. The new sulfuric alkylphenolate additives - medium (AKI-144d) and high alkaline (AKI-154d) additives are obtained from the environmentally friendly method - sulfurisation of dodecylphenol with sodium sulfide.

It has been established that sulfur-containing AKI-144d based on dodecylphenol is superior to AKI-144 additives based on alkylphenol (R = C_8-C_{12}) due to corrosion, oxidation properties and water resistance.

The anti-oxidation properties of AKI-144d were also studied by modeling manometric method and showed that AKI-144d increased its induction period compared with the AKI-144 additives, which means, its anti-oxidant properties are more superior.

The dependence of the newly acquired variety on the structure of the properties of multifunctional alkylphenolate additives containing nitrogen, sulfur and various functional groups was studied.

Dodecylphenol, formaldehyde, ammonia and amino (or p-aminobenzoic) acid condensation products of calcium salts AKI-31 (AKI-57) additives and thermal stability were studied in the OD-102T type Paulik and Paulik Erdei systemic derivatograph. It has been shown that the thermal stability of phenyl radical additives AKI-57 is greater than that of AKI-31 additives and IXP-114 and ASC additives.

The amino acidification reaction was obtained with new additives AKI-31 and AKI-172 and approved by the patent.

A new medium and high alkaline carboxylate group containing alkylsalicylate type and other alkylphenolate additives were obtained by simple method.

M-8V, M-10G_2, M-12VB, M-14G_2, engine oils were produced using synthesized additives and commodity additives, which are up-to-date with foreign Shell oils, and meet and modern requirements.

Practical significance. New medium and high alkylphenolate additives − AKI-144d and AKI-154d, have been obtained from

dodecylphenol, that are not corrosive to equipments and is environmentally friendly.

Antiorrosion, anti-oxsidation and detergent properties of synthesized medium alkali additives are superior to the foreign analogues MASC, VNIINP-714 and OLOA-218A, and high alkylpheolate additives (AKI-154d, AKI-156d, AKI-172, AKI-174, etc.) exceed their foreign analogues ASC, CIATIM-339 for anticorrosion properties.

Obtained calcium salts (AKI-31 and AKI-57) of the condensation product of dodecylphenol, formaldehyde, ammonia and amino acids (or p-aminobenzoic acid) have high thermal stability and according to this thermal stability and functional properties they exceed analogues IXP-114, CIATIM-339 and ASC.

The new range of the synthesized high alkaline multifunctional alkylphenolate additives that contain heteroatoms and various functional groups exceed foreign analogues for anticorrosion properties.

Having synthesized according to the simple method, efficient and high alkaline additive AKI-156d is recommended for industrial application.

On the basis of synthesized additives that meet modern requirements oil compositions M-8V, M-10G_2, M-12VB, M-14G_2 have been created. The quality indicators of engine oils are the same as their foreign analogues of Shell engine oils.

It is found that when switching from medium alkaline to high alkaline additives, these additives the quality of engine oils do not deteriorate, that allows to reduce the quantity of the additive and replace MASC additive, which is expensive and technologically hard obatined.

Author's personal presence. The issue of dissertation work, experimentation, analysis of the obtained results and generalizations were done by the author himself.

Publication. Published 31 scientific papers have been published on dissertation work, including 2 patents, 12 articles (5

abroad). 17 abstracts of reports made at international and national conferences were published and awarded with 12 certificates.

Proof of work and published works. Proceedings of the II Republican Conference "Organic Reagents in Analytical Chemistry"dissertation results , dedicated to the 100th anniversary of professor A.A.Verdizadeh's birth (Baku-2014); the role of a multidisciplinary approach to addressing current problems of fundamental and applied sciences (location, technical and chemical sciences) (Baku-2014); International Multidisciplinary Forum of Academic Science Week, dedicated to the 70th anniversary of ANAS (Baku-2015); "Alternative sources of raw materials and fuel", V and VI International Scientific and Technical Conference "AIST-2015" and "AIST-2017"; Republican Scientific Conference on "Lubricants, Fuels, Special Liquids, Additives and Reagents", dedicated to the 50th anniversary of the Institute of Chemistry of Additives after academician A.M. Guliyev (Baku-2015); Integration processes of the world science in the 21st century, book of abstracts (Ganja-2016); Forth Annual İnternational Conference on Chemistry, Chemistry abstracts (Athens, Greece-2016); International Conference on Actual Problems of Contemporary Chemistry and Biology, dedicated to the 93rd anniversary of national leader H.Aliyev (Ganja-2016); IX Baku International Mamedaliyev Conference on Petrochemistry (Baku-2016); Materials of the Republican scientific conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev (Baku-2016); International scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems" dedicated to the 100th anniversary of academician B.K. Zeynalov (Baku-2017); Proceedings of the International Scientific Conference "Functional Monomers and Specific Polymeric Materials: Challenges, Perspectives and Practical Views" (Sumgait 2017); Actual problems of modern nature and economic sciences. Proceedings of the International Scientific Conference (Ganja-2018); International scientific-practical conferences on the 110th anniversary of Academician V.Aliyev "Prospects for innovative development of oil refining and petrochemistry" (Baku-2018); XXXI International scientific and

technical conference "Chemical reagents(agents), reagents and processes of small-tonnage chemistry" REACTIVE-2018 "(Belarus, Minsk-2018); the materials of the scientific conference "Naghiyev's Readings", dedicated to the 110th anniversary of the academic Murtuza Naghiyev (Baku-2018) also have been reported.

The volume and structure of the dissertation. The dissertation consists of Introduction, 5 chapters, results, list of literature with 249 sources of literature, 12 figures, from printed material on 172 pages covering 40 tables, appendices (act, spectra, AKI-156d additives and 12 certificates), 204550 characters.

The introduction presents and justifies the urgency of the challenges faced by modern high-quality motor oil production, ways to solve them, the purpose of the work, scientific novelty, and practical significance.

Chapter 1 provides a review of the literature, the modern requirements for motor oils, their production and consumption status, and the synthesis of multifunctional alkylphenolate additives used to enhance the properties of motor oils.

The challenges faced by increasing demand for engine oils and their solutions were analyzed.

Chapters 2 and 3 discuss the results obtained from the synthesis and study of alkylphenols and their intermediate and high alkylphenolate additives used in said chapters.

Chapter 4 deals with the practical part.

Chapter 5 is dedicated to the creation of new engine oils M-8V, M-10G_2, M-12VB and M-14G_2 using synthesized medium and high alkylphenolate additives.

At the end of the dissertation are summarized the results of the research, a list of references and appendices.

BASIC CONTENT OF WORK

Synthesis of modifications of moderate alkylphenolate additives

The alkylphenols R = C_8 – C_{12} and R_{12} from polymer-distillate phenol catalyst KU-2 with the presence of catalyst KU-23 were used to

obtain new alkylphenolate additives as primary raw materials. Synthesized medium additives:

1. **AKI-144d** − didodesyl (dioxybenzyl) sulfide calcium salt;

2. **AKI-34** – calcium salt of the formaldehyde and dodecylmercaptan condensation product of methylenbisdodesylphenol;

3. **AKI-91 (AKI-90)** – calcium salt of the condensation product of formaldehyde and dodecylmercaptan amine di(hydroxydesylbenzyl) amide;

4. **AKI-31 (AKI-57)** – calcium salt of condensation product of formaldehyde and amino acid (p-aminobenzoic) amino di (hydroxydesylbenzyl);

5. **AKI-146d** – calcium salt of condensation product the formaldehyde and p-aminobenzoic acid of methylenbisdodesylphenol;

6. **AKI-171** − calcium salt of dodecylphenol formaldehyde, monoethanolamine and salicylic acid condensation product;

7. **AKI-173** − calcium salt of condensation product of formaldehyde, monoethanolamine and salicylic acid of dodecylphenol;

8. **AKI-44 (AKI-48)** – Calcium salt of the formulation of methylenbisdodesylphenol with formaldehyde and butylamine (desylamine);

9. **AKI-1 (AKI-2, AKI-3, AKI-4**) – calcium salt of condensation product of dodecylphenol with formaldehyde and ethylenediamine (diethylentriamine, tetraethylenpentamine, hexamethylenediamine).

The challenges faced by the increasing demand for engine oils and their solutions have been analyzed.

Sulfur-preserving alkylphenolate additive

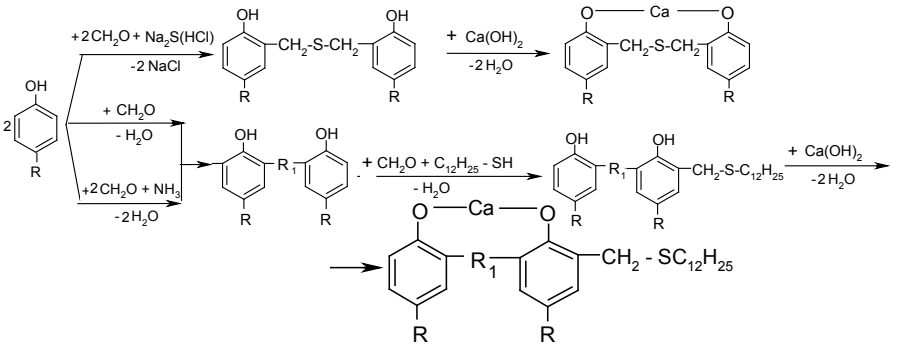
Sulfur-containing alkylphenolate additives are divided into two main groups:

1. Additives of sulfur atoms located between aromatic rings

2. Additives that store sulfur atoms in alkyl radicals

In motor oils, sulfur atoms are most commonly used in additives, which are located between aromatic rings. In the known sulfurization process, sulfur chloride and elemental sulfur are used as sulfur agents. Elementary sulfur is preferred over sulfur chloride because it is stable, not harmful, does not corrose, is easy to store and transport [1].

We developed new AKI-144d supplement with the use of sodium sulfide as a sulfurizing agent [5]. It differs from the environmentally friendly (without hydrogen chloride and hydrogen sulfide separation), energy savings (thiometry reaction at 90-95^{0}C instead of the sulfur reaction of 170-180^{0}C) and the technology of extraction



R−C_8−C_{12} − AKI-144; C_{12} −AKI-144d
R−C_{12}, R_1−CH_2− AKI−34
R – C_{12}, R_1−CH_2−NH−CH_2− AKI−91

Alkylphenol (R–C_8–C_{12}; C_{12}) is condensed with formaldehyde and sodium sulfide, neutralized with calcium hydroxide, dried, and then separated from the additive mechanical mixture.

The AKI-34 and AKI-91additives located in the alkali radical of sulfur atom were also obtained [3, 15, 18].

Table 1 shows that AKI-144 and AKI-144d additives significantly reduce the corrosion, anti-oxidation, washing properties

[1] Селезнева, И.Е. Детергентно-диспергирующие присадки к моторным маслам / И.Е.Селезнева, А.Я. Левин, С.В.Монин // Химия и технология топлив и масел, − Москва: − 1999. № 6, − с.39-43

and wear diameters of the M-8 oil, with the corrosion and oxidation properties of CIATIM-339 and IXP-101 and is superior to IXP-114 additives with its wear property.

Table 1

Physical-chemical and functional properties of AKI-144, AKI-144d, AKI-34 and AKI-91 additives

Additives and oil	Physical-chemical property of the additive				M-8 oil+5% additive			
	Alkaline number, mgKOH/g	Kinematic viscosity, at 100^0C, mm^2/s	Sulfate ash %	Washing with water, (with 10% additive)	Corrosion, (lead plates), g/m^2	Stability on induction period for sludge formation, (by IPO, 30h.) sludge,%	Detergent properties, (PVC), point	Wear resistance (wear spot-diameter), mm
M-8 oil	–	–	–	–	180.5	2.5	6.0	0.95
AKI-144	72.4	74.3	7.1	25	9.4	0.75	0.5-1.0	0.45
AKI-144d	75.2	72.2	7.4	15	4.9	0.47	0.5	0.42
AKI-34	80.0	70.1	7.7	–	3.5	0.39	0.5	0.40
AKI-91	82.8	69.6	7.5	–	2.5	0.37	0.5	0.38
*CIATIM-339	42.0	–	10.3	–	21.4	3.4	0.5	–
IXP-114	89.4	71.1	8.34	18	2.4	0.45	0.5	0.55
IXP-101	64.8	56.8	12.0	65.5	18	4.2	0.5-1.0	–

*10% additive

As one of the main components of motor oils is the alkylphenolate additives, their water-resistant properties are of great importance as the content of motor oils is reduced when the additives are washed with water and the oil quality is low.

AKI-144d, based on dodecylphenol, is superior to AKI-144 additives based on alkylphenol ($R\text{-}C_8\text{-}C_{12}$) with functional properties and water resistance. This is due to the adverse effects of low molecular weight, alkylphenol fragment ($R\text{-}C_8\text{-}C_{12}$) on the AKI-144 additives, poor soluble fat and water-washed 7% butylphenol additives.

The additions AKI-34 and AKI-91, which contain the sulfur atom in the alkyl radical, are superior to their anti-corrosion

properties compared to the AKI-144 and AKI-144d additives. This is explained by the fact that the spatial effect produced by alkyl radicals is smaller than that of aryl radicals, and the sulfur atom in alkylsulfides easily forms a protective layer for metals.

When comparing AKI-91 and AKI-34 additives, it is clear that the anti-corrosion effect of AKI-91 is greater than that of AKI-34, as it contains more nitrogen atoms.

Investigation of AKI-144 and AKI-144d as oxidative inhibitors

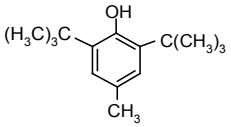
The anti-oxidant properties of synthesized AKI-144 and AKI-144d have been studied in the oxidation reaction of izopropylbenzene on manometric devices.

The ability of AKI-144 and AKI-144d to react with cumulperoxide radicals has been investigated. For this purpose, a model reaction of hydrocarbon oxidation was used and a detailed study was performed.

When analyzing the values of kinetic curves and kinetic parameters, f and K_7 (Table 2), it appears that AKI-144d has high oxidation resistance. This additive repeatedly breaks the oxidation chain (f = 7.2) and is highly responsive to cumulperoxide radicals. (K_7=5.62·10^4 mol/l^{-1}·s^{-1}).

Table 2

Kinetic parameters characterizing the oxidative properties of synthesized AKI-144d and AKI-144 additives

Additives	T=60^{0}C		T=110^{0}C
	Ƒ	k_7·$^{-4,}$, l.mol^{-1}s^{-1}	τ^1 ,min.
AKI-144d	[InH]=5·10^{-5}mol/ l 7.2	5.62	[InH]=5·10^{-5}mol/ l 250
AKI-144	[InH]=5·10^{-5}mol/ l 2.5	2.80	[InH]=5·10^{-5}mol/ l180
Ionol 	2.00	2.10	150

Thus, AKI-144d is known for its anti-oxidant properties superior to that of ionic acid.

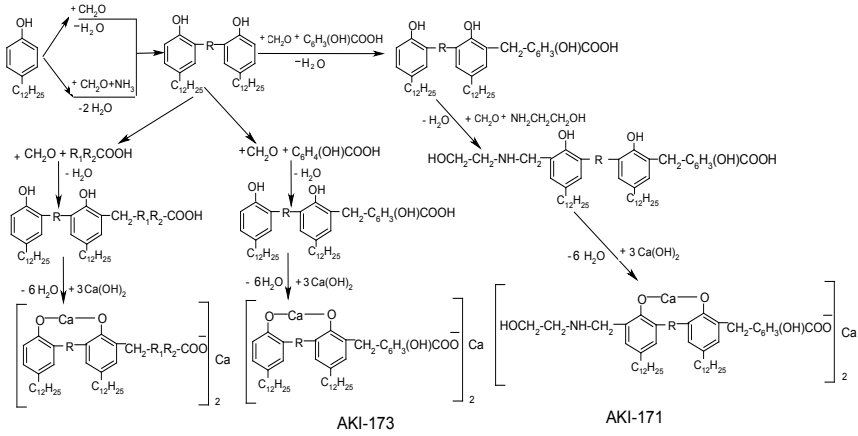
Carboxylate group, nitrogen and sulfur-containing alkylphenolate additives

Alkylsalicylate additives have high detergents, anti-oxidation properties and thermal stability, but alkylsalicylate additives are expensive because of their multi-step and difficult to obtain technology [2].

At the same time, they are used in various groups of engine oils because of their high quality.

New multifunctional AKI-171 and AKI-173 additives have been purchased to improve the corrosion, anti-oxidation and detergent properties of motor oils[6, 10, 20, 28].

The synthesis scheme of the additive is as follows:



R–CH_2–, R_1R_2–NHC_6H_4− AKI-146d; R–CH_2−NH−CH_2–, R_1R_2–SCH_2− AKI-90, R–CH_2−NH−CH_2–, R_1R_2–$NHCH_2$− AKI-31; R–CH_2−NH−CH_2–, R_1R_2–NHC_6H_4− AKI-57; R–CH_2− AKI-171; R–CH_2−NH−CH_2− AKI-173.

Other condensation products and their salts may be obtained.

Initial ingredients for obtaining highly addictive additives were obtained under different conditions and optimal acquisition

[2] Гордаш, Ю.Т. Алкилсалицилатные присадки к моторным маслам // − Москва:Нефтепереработка и нефтехимия, − 1992. №7, − с.43-45

conditions were found. The structure of the synthesized substances was confirmed by the IR-spectrum analysis method.

Work has been carried out to obtain low-quality alkylsisylate-type additives obtained by easy technology, and additives AKI-31, AKI-57, AKI-90, and AKI-146d, which contain carboxylate fragments, have been obtained by gradual condensation. At each stage, the products obtained were investigated and their structure was studied using IR-spectral analysis [16, 19, 24, 29, 30].

Table 3 lists the ASC, CIATIM-339, IXP-101, and IXP-114 additives obtained in laboratory conditions for comparison.

Table 3

Physical-chemical and functional properties of additives

Addditive examples	Alkaline number, mgKOH/g	Sul-fate ash, %	Kinematic viscosity, 100^0C, mm^2/s	M-8 oil content with additives, 4 mgKOH/g		
				Corrosion, (lead plates), g/m^2	Stability on induction period for sludge formation, (by IPO, 30h.) sludge,%	Deter-gent proper-ties, point
AKI-171	115.0	9.7	76.8	1.2	0.88	0.5
AKI-171	114.4	9.68	78.5	1.5	0.82	0.5
AKI-173	87.4	9.1	80.2	2.3	0.78	0.5
AKI-173	85.1	9.0	78.8	2.8	0.81	0.5
AKI-31	96.5	12.5	83.4	1.5	0.1 40s 0.2 50s 0.5	0.5
AKI-57	95.4	11.8	83.4	1.2	0.30	0.5
				*1.8	0.35	–
AKI-90	97.5	10.1	85.1	3.5	0.25	0.5
AKI-146d	82.4	8.4	94.8	1.4	0.35	0.5
				*3.5	0.45	–
ASC	56.4	7.5	–	35.1	0.8	0.5
CIATIM-339	42.0	10.3	–	31.4	3.5	0.5
IXP-101	64.8	12.0	56.8	15.0	3.2	0.5
IXP-114	89.4	8.34	71.1	2.4	0.45	0.5

*Additive in 3% thickness

Based on the combination of alkylphenol, carboxylate fragment and nitrogen atom in the additives AKI-31, AKI-57, AKI-90 and AKI-146d are superior to CIATIM-339, IXP-101 and ASC trademarks for their corrosion and oxidation properties, and are at the same level with IXP-114 additive.

The synthesized AKI-146d, AKI-31 and AKI-57 additives are effective multifunctional additives. The quality of the AKI-146d additive lags far behind the AKI-57 additive. Thus, the corrosion and oxidation resistance of the 3.0% fat sample of AKI-146d is 3.5g/m^2 and 0.45%, and the AKI-57 additives are 1.8g/m^2 and 0.35%. In our opinion, this is because AKI-57 additives contain additional nitrogen atoms.

The anti-corrosion properties of the AKI-171 and AKI-173 additives are superior to those of the commercial additives, the oxidizing properties are the same as those of the ASC additives and the IXP-114 additives.

AKI-31 and AKI-90 additives differ in heteroatoms. AKI-31 additives were obtained with amino acid and AKI-90 additives with mercaptic acid. Their properties are practically the same, the wear properties of AKI-90 are slightly higher than AKI-31 additives. Studies show that these additives have a multifunctional nature.

It is possible to meet the requirements of modern machinery with the use of modern engine oils with the use of additives with high quality and high thermochemical properties. Therefore, the thermal oxidation properties of high quality AKI-31 and AKI-57 additives have been studied. Thermo-analytical studies were conducted on the OD-102T type derivatographer Paulik, Paulik Erdei system (Hungary), dynamic mode with 10°C/min heating rate in air.

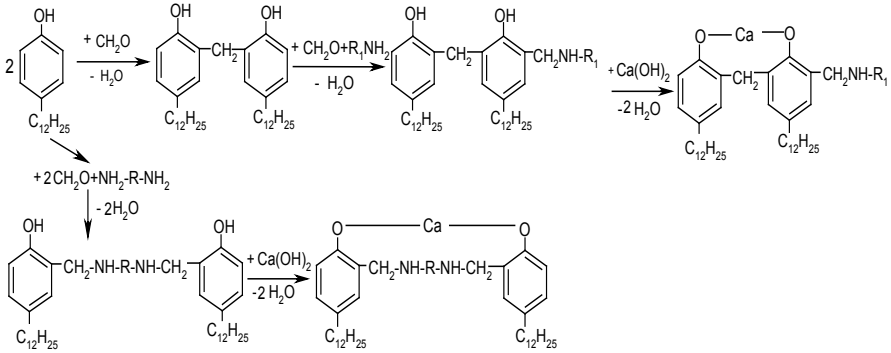
Studies show that AKI-57 and AKI-31 additives have high thermal stability. Thus, the presence of phenyl radicals in AKI-57 additives increases its thermostability to 10°C compared to AKI-31.

ASC and IXP-114 additives, which contain carboxylate groups or nitrogen atoms, are far behind in the term of thermostability of both AKI-31 and AKI-57 additives (which contain both the carboxylate group and the nitrogen atom).

Nitrogen-containing alkylphenolate additives

To study the effect of alkyl radicals, the number of nitrogen atoms and their distance to each other, the use of long and short chain amines (butylamine and desilamine) (AKI-44 and AKI-48) [8], ethylenediamine, diethylentriamine, tetraethylenpentamine, and hexamethylamine. AKI-1, AKI-2, AKI-3 and AKI-4) have been synthesized [1, 2].

Expected formulas for additives are as follows:



Other condensation products and their salts may also be obtained.

$R{-}CH_2\text{-}CH_2{-}$ AKI-1; $R{-}(CH_2\text{-}CH_2)_2NH{-}$ AKI-2;
$R{-}(CH_2{-}CH_2)_4(NH)_3{-}$ AKI-3; $R{-}(CH_2\text{-}CH_2)_4{-}$ AKI-4;
$R_1{-}C_4H_9{-}$ AKI-44; $R_1{-}C_{10}H_{23}{-}$ AKI-48

AKI-1, AKI-2, AKI-3 and AKI-4 additives were obtained from the combined condensation of dodecylphenol, formaldehyde and amines, and the AKI-44 and AKI-48 additives without condensation. The physico-chemical and functional properties of additives obtained in the optimal variant are given in Table 4. The synthesized additives significantly improve the quality of M-8 oil.

Studies show that depending on amino radicals, the functional properties of AKI-44 additives are slightly higher than AKI-48

additives. This is explained by the fact that it contains a long alkyl radical amino group in the aromatic ring and reduces its activity [8].

AKI-44 and AKI-48 additives are superior to CIATIM-339, IXP-101 and ASC, due to their corrosion and oxidation properties and is at the same level with the IXP-114 additive.

Comparing AKI-1, AKI-2, AKI-3 additives, the advantage of AKI-3 additives for corrosion and oxidation is that it contains five nitrogen atoms, with higher adsorption properties [14, 22]. Thus, additives AKI-1 and AKI-2 contain two and three nitrogen atoms.

Compared to the AKI-1 and AKI-4 additives, the nitrogen atoms in the 1,2-visinal state are superior to the AKI-4 additives in the 1,6-terminal state due to their corrosion and oxidation properties. This is most likely due to the higher adsorption properties of the nitrogen atoms in 1,2 positions [13].

Table 4

Physical-chemical and functional properties of additives

Additive samples	Alkaline number, mgKOH/g	Sul-fate ash %	Kinematic viscosity, 100^0C, mm^2/s	M-8 oil content with additives, 4mgKOH/g			
				Corro-sion (lead plates), g/m^2	Stability on induction period for sludge formation, (by IPO, 30h.) sludge, %	Wear resis-tance (wear spot-diame-ter), mm	Deter-gent proper-ties, (PVC), point
M-8 oil (w/o additive)	–	–	–	180.5	2.5	0.95	6.0
AKI-44	84.1	7.5	68.9	3.2	0.16	–	0.5
AKI-48	79.6	7.1	64.4	8.5	0.45	–	0.5
AKI-1	138.1	9.7	75.2	7.2	0.82	0.37	0.5
AKI-2	142.8	10.1	80.1	3.2	0.68	0.38	0.5
AKI-3	146.7	10.6	132.2	1.7	0.25	0.56	0.5
AKI-4	90.5	8.3	125.6	16.2	1.05	–	0.5
IXP-101	64.8	12.0	56.8	15.0	3.2	0.7	0.5
IXP-114	80.1	7.6	68.1	2.8	0.47	0.50	0.5
CIATIM-339	42.0	10.3	–	31.4	3.5	0.5	0.5
ASC	56.4	7.5	–	35.1	0.8	–	0.5-1.0

*The wear properties of the additives are determined by 5% additive.

The synthesized additives significantly improve the quality of M-8 oil.

Parts and engines are exposed to rust and corrosion due to humidity and various weather conditions during storage.

In recent years, metal-based compounds have been used extensively as protective additives to fat. The protective properties of AKI-1, AKI-2 and AKI-3 additives have also been studied [17].

Humidity and the relative air indices of the additives to the complex system of research based on the qualification tests of fat protection properties were studied according to GOST 9.054-75 1, 4, 5. Corrosed areas were observed in three ways (with steel plates).

Studies show that nitrogen-fixing AKI-1, AKI-2, AKI-3 alkylphenolate additives have protective properties, and the protective properties of AKI-3 additives are superior to AKI-1 and AKI-2 additives. Thus, the starting time of corrosion centers with oil AKI-3 additives is observed on the 5th day and corrosion of steel plates is 13%, 2nd method is 45%, and third method is 32%.

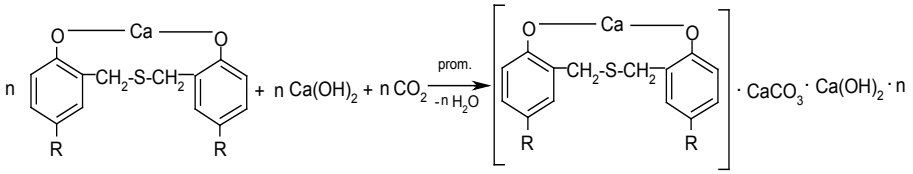
The fungicidal and bactericidal properties of these additives have also been studied (2 types of bacteria and 5 types of fungi). Studies show that additives have no resistance to bacteriuria and fungi.

Synthesis and research of alkylphenolate additives with high alkaline colloidal structure.

One of the ways to improve the quality of additives is to increase their alkaline numbers. Alkaline-rich additives have high neutralization properties, neutralizing acids caused by oxidation of fat, and increasing their resistance to oxidation and corrosion. Initial stages of the synthesis of high alkylphenolate additives correspond to the synthesis of alkali additives but only by the process of carbonation. Their synthesis has been studied in detail before the neutralization process, where more than stheiometric calcium hydroxide is used in the neutralization process, the promoter is added and carbonation is carried out. Promotor can be given in both neutralization and carbonation. Highly alkaline additives are not obtained without promoters.

Using the condensation product of the AKI-144d additive and excessive Ca $(OH)_2$ and promoter, after 4-5 hours of neutralization, carbon dioxide is released at 85°C for 4-4.5 hours, the carbonation product is dried and separated from centrifuges by mechanical impurities, high alkaline **AKI-154d** additives − carbonated calcium salt of didodesyl (dioxybenzyl) sulfide were obtained [9].

The reaction scheme of AKI-154d alkylphenolate additives is as follows:

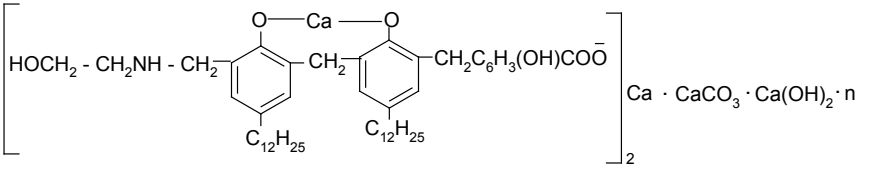


$R-C_{12}$

AKI-154d supplement was obtained with various promoters - acetic acid, glycerol, dietanolamine, ethylene glycol.

Studies show that the use of dietanolamine as a promoter has a higher alkaline content and quality in additives.

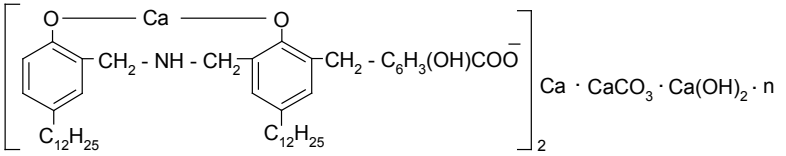
Carbonated variants − AKI-172 and AKI-174 have been obtained to improve the functional properties of salicylate-type AKI-171 and AKI-173. Proposed formula of AKI-172:



AKI-172 is a calcium salt of the condensation product of methylenbisdodesylphenol, formaldehyde, salicylic acid and monoethanolamine [11, 23, 31].

AKI-174 is a carbonated calcium salt of the condensation product of formaldehyde and salicylic acid amino dioxide (hydroxydodylbenzyl) [4, 21].

Expected formula of the formula is as follows:



High-affinity AKI-172 and AKI-174 additives were obtained using glycerin as a promoter.

The physical-chemical and functional properties of the AKI-154d, AKI-172 and AKI-174 additives are shown in Table 5.

Table 5

Physical and chemical additives AKI-154d, AKI-172 and AKI-174 and functional properties

Additives	Alkaline additives, mgKOH/g	Sul-fate ash, %	M-8 oil + 5% additive		
			Corrosion. (lead plates) g / m^2	Stability on induction period for sludge formation, (by IPO, 30h.) sludge,%	Detergent properties, (PVC), point
AKI-154d	162.4	16.8	1.5	0.25	0-0.5
AKI-172	163.6	18.2	0.1	0.4	0-0.5
AKI-174	155.2	16.9	0.15	0.3	0-0.5
VNIINP-714	155.0	20.5	7.5	0.47	0.5
OLOA-218A	147.0	17.6	9.8	0.45	0.5
MASC	140.0	16.8	4.5	0.40	0.5

Additives VNIINP-714, OLOA-218A, MASC and AKI-144d, AKI-171, AKI-173 are also included in the table for comparison. After carbonation, AKI-144d, AKI-171, and AKI-173 additives possess increased oxidation, corrosion and detergent properties.

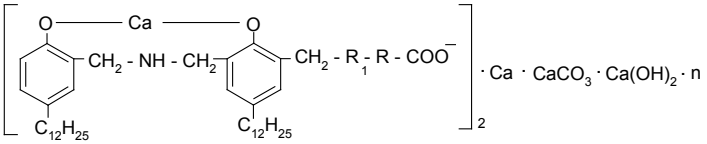
The results of the test showed that AKI-154d, AKI-172 and AKI-174 additives have high functional properties and are superior to foreign VNIINP-714, OLOA-218A and MASC additives due to their corrosion properties.

High alkaline nitrogen-sulfur and carboxylate retention alkylphenolate additives

Modified alkylphenolate additives − carbonated variants of the alkylsalicylate type alkaline type AKI-31, AKI-57 and AKI-90 containing simple heteroatoms and carboxylate groups were obtained.

Condensation products of formaldehyde and amino acids (p-aminobenzoic or thioglycol) amino di (hydroxydesylbenzyl) amine carbonated calcium salts-AKI-124, AKI-134, and AKI-112 additives have been synthesized and studied (Table 6) [7, 12, 25, 27].

The intended formula for the additives is as follows:



here $R_1R{-}S{-}CH_2{-}$ (AKI-112); $R_1R{-}NH{-}CH_2{-}$ (AKI-124); $R_1R{-}NH{-}C_6H_4{-}$ (AKI-134)

Table 6

Physical-chemical and functional properties of additives AKI-112, AKI-124 və AKI-134

Additives	Alkaline number, mgKOH/g	Kinematic viscosity, 100^0C, mm^2/s	Sul-fate ash, %	M-8 oil + 5% additive		
				Corrosion (lead plates), g / m^2	Stability on induction period for sludge formation, (by IPO, 30h.) sludge,%	Detergent proper-ties, (PVC), point
AKI-112	138.1	72.2	14.2	1.2	0.40	0.5
AKI-112	134.8	73.8	13.9	2.4	0.45	0.5
AKI-124	147.8	70.1	16.4	0.6	0.2	0.5
AKI-124	144.6	64.4	16.0	0.7	0.15	0.5
AKI-134	145.2	72.2	16.1	1.0	0.22	0.5
AKI-134	150.1	74.8	16.6	0.9	0.24	0.5
VNIINP-714	143.0	–	17.2	6.4	0.41	0.5
OLOA-218A	147.0	–	17.6	9.8	0.45	0.5
MASC	140.0	–	16.8	4.5	0.40	0.5

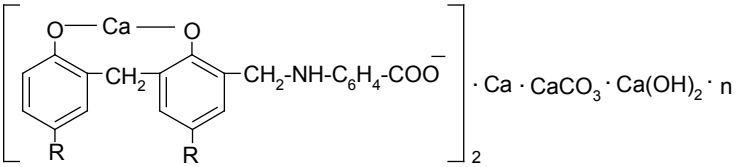
The table shows that AKI-112, AKI-124 and AKI-134 are multi-functional additives, and their anti-corrosion properties are superior to VNIINP-714, OLOA-218A and MASC additives.

The results show that the effect of carboxylate, alkylphenolate groups on the molecule of additives combined with two nitrogen atoms and the stable colloidal dispersion in carbonation contribute to its improved properties.

AKI-156d is a carbonated calcium salt of the formaldehyde and p-aminobenzoic acid condensation product of high-alkaline alkylphenolate additives that contain nitrogen and carboxylate [26].

To obtain AKI-146d additive carbon dioxide, AKI-156d additive the optimization of AKI-146d supplementation was performed by neutralizing the calcium hydroxide promoter glycerol with 40% (according to dodecylphenol) followed by carbonation..

The formula of AKI-156 and AKI-156d additives is as follows:



$R-C_8-C_{12}$(AKİ-156); C_{12} (AKİ-156d)

Studies show that high quality alkaline additives are obtained using dietanolamine as a promoter to obtain high alkaline additives and glycerol or ethylene glycol for nitrogen-fixing additives. AKI-156d is self-absorbing, alkaline quantity is 140-165mg/h, sulfate ash is 15.5-17.5 mm^2/h.

The physical-chemical and functional properties of AKI-156d additives and additives VNIINP-714, OLOA-218A and MASC are given in Table 7.

Oxidation stability is considered to be brought about going up to 0.5%.

As can be seen from the table, the anti-corrosion properties of AKI-156d are superior to the additives VNIINP-714, OLOA-218A and MASC.

AKI-156d add-on can be noted for easy acquisition technology and quality (Table 7).

Table 7

Physical-chemical and functional properties of additives AKI-156d

Names of indicators	AKI-156d addi-tive	OLOA-218A	VNIINP-714	MASC	Trial method, GOCT	ASTM
Kinematic viscosity, 100^0C, mm^2/s	65.5	–	–	–	33	D 445
Sulfate ash, %	16.5	18.0	205	16.8	12417	D874
Alkaline number, mgKOH/g,	155.2	147.0	155.0	140	11362	D-4739
Mass fraction of mechanical impurities,%,	0.2	–		–	6370 and this T.C. 5.2.b	D-2273
Water share,%	0.15	–		–	2477	–
Flash temperature, ^{0}C Open caste	150	–		–	4333	D-92
Mass content of calcium,%	4.5				13538	–
$M\text{-}8_{Baku}$ oil+ 5% additive						
Depletion Stability Induction Stability (IPO 30 hours), Depletion, 0.5%, no more than	Holds	holds	holds	holds	11063	D-1500
Corrosion, (in lead plates), g/ m^2	0.38	9.8	2.5	4.5	20502	D-665
Detergent properties, (PZV), score, not too much	0.5	0.5	0.5	0.5	5726	D-892
Solubility in oil	full	full	full	full	full	–

Production of AKI-156d additives can be made on technical industrial installation at the High Technologies Park of Azerbaijan National Academy of Sciences.

Production technology of AKI-156d additives based on laboratory studies

P-1 reactor with mixer and X-1 coolant with 100kg alkylphenol from H-1 pump and D-1 dispenser, 20kg 35-37% formalin with D-2 dispenser by H-2 pump, 2kg Ca (OH) 2 catalyst with D-3 dispenser from E-3 capacity is given. From E-4 container with H-4 pump through D-4 dispenser 9kg p-aminobenzoic acid is given and at 80-85°C for 1.5-2.0 hours stir the mixture mixture's refraction coefficient is 1.5160-1.5180 and the condensation is stopped and the product is separated from water by adding 50kg I-20A oil from the E-5 container H-5 pump D-5 dispenser.

Condensation solution dissolved in I-20A oil is transferred to P-2 reactor with H-6 pump and in this reactor a 3kg promoter (glycerin) at 85°C is added, then the suspension of 40kg calcium hydroxide in 80-90kg Autol oil is added gradually for 3-4 hours from E-6 container D-6 dispenser the product neutralization is continued for 3 hours.

Then to the same reactor carbon dioxide is supplied at 22.5 l/min at 85°C through E-7 container and during this temperature, 4.5 hours of carbonation is carried out.

The carbonated product is transferred to the T-1 heater with the H-7 pump, dehydrated, and transferred to the M-1 settler(precipitator) by the E-3 container. After the M-1(settler) precipitator, C-1 is sent through first-rate (level) centrifuge to remove any initial mechanical impurities. The product is then transferred to a K-1 vacuum unit to drain the water and dry any moisture. Drying of the additive in the column (0.072-0.092mPa) is carried out under pressure and at no more than 130°C.

After drying the mixture is transferred to the C-2 centrifuge to be completely rid of the impurities. According to the analysis, when the mechanical impurity of the additive is less than 0.1%, it is released into the vat through the H-8 pump (figure 1).

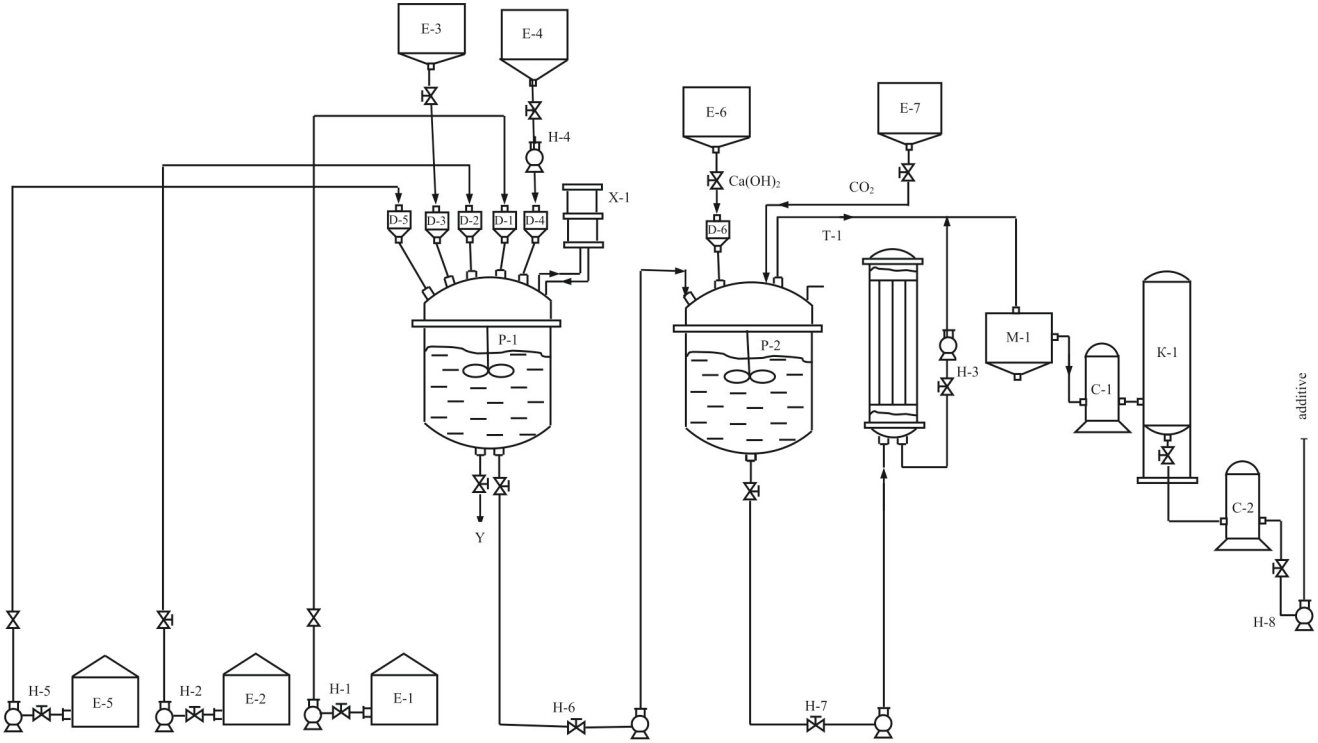


Figure 1. Process flow diagram of industrial AKI-156d additive.
P-1, P-2 – reactors; X-1 – cooler (coolant); E-1, E-2, E-3, E-4, E-5, E-6, E-7 – container; H-1, H-2, H-3, H-4, H-5, H-6, H-7, H-8 – pump; D-1, D-2, D-3, D-4, D-5, D-6, D-7 – dispenser; T-1 – heater; M-1 – settler (precipitator); C-1, C-2 – centrifuge; K-1 – vacuum unit

Production of modern motor oils of various purposes

The main component of oils produced in Azerbaijan is IXP-101 additives. As the additive is barium salt, high ash, low alkaline and corrosion protection effect is poor. Therefore, it is impossible to create modern engine oil with its use. In addition, due to the low solubility of base oils in Azerbaijan, methacrylate industrial additives - Viscoplex 2-670 and PMA"D" were used to increase motor oil viscosity, and Viscoplex 5-309 was used to lower the freezing temperature.

Using new medium and high aluminum AKI-31, AKI-57, AKI-144d, AKI-146d, AKI-154d, AKI-156d, etc. Additives and industrial additives DF-11, Dneprol, C-5A, C-150, C-400, IXP-114, ASC, Viscoplex 2-670, Viscoplex 5-309 the motor oils M-8V, M-12VB, M-10G_2, M-14G_2 were created.

New compositions of M-8V engine oil:

1. M-6_{Baku},Viscoplex 2-670, AKI-31 (or AKI-57), DF-11, C-150, C-5A, Viscoplex 5-309, PMC-200A.
2. M-6_{Baku} oil, Viscoplex 2-670, AKI-172 (or AKI-174), DF-11, C-150, C-5A, Viscoplex 5-309, PMC-200A.
3. M-6_{Baku} oil, Viscoplex 2-670, AKI-156d (or AKI-154d), DF-11, C-150, C-5A (or Dneprol), Viscoplex 5-309, PMC-200A.

New compositions of M-12VB engine oil:

Requirements for engine oils M-$12B_2$ and M-12VB are the same, except that they differ in the viscosity index. Thus, the M-$12B_2$ motor oil viscosity index should not be less than 80, and the M-12VB motor oil viscosity index should not be less than 77.

1. M-$11_{Eastern}$ oil, AKI-57, DF-11, C-150, PMC-200A.
2. M-10_{Baku} oil, Viscoplex 2-670, AKI-146d, DF-11, PMA”D”, C-150, PMC-200A.
3. M-10_{Baku} oil, Viscoplex 2-670, AKI-156d, C-150 (C-400), DF-11 Viscoplex 5-309, PMC-200A.
4. M-$11_{Eastern}$ oil, AKI-174, C-150, DF-11, PMC-200A.

The physical-chemical and functional properties of M-8V and M-12VB oils are given in Table 8.

Table 8

Physical-chemical indicators and test results of M-8V and M-12VB oils comparable to foreign analogs

Names of indicators	GOCT 10541 -78 (norm)	M-8V oil		M-12VB oil			M-12VB type Shell oil Rotella X30
		con-tent 3	M-8V type Shell oil Rimula C20W-20	T.C. 3536814 -008-2004 (norm) M-12VB	T.C. 38 1011198 -89 (norm) M-12V$_2$ oil	Con-tent 3	
Kinematic viscosity, 100^{0}C, 0^{0}C,mm^2/s	8±0.5	8.3-8.4	8.8	11.5±13.0	10.5±13.0	11.7-12.1	11.8
Viscosity index, no less than	93	94	102	77	80	82	60
Alkaline number, mgKOH/g, no less than	4.0	6.6-6.8	4.0	5.0	5.0	9.1-9.2	6.4
Sulfate ash,%, no more than	0.95	0.93	0.65	1.3	1.3	1.2-1.25	0.8
Flash tempera-ture,^{0}C, open caste, no more than	200	212	241	205	205	210	238
Freeze tempera-ture, ^{0}C, no more than	Minus 25	Mi-nus 25	Minus 25	Minus 15	Minus 15	Minus 15	Minus 24
Stability of the sedimentation induction period (IPO 30 hours), holds	30	40	40	30	30	30	30
Corrosion, (in lead plates), g / m2, no more than	10	no	no	10	10	no	no
Detergent prop-erties, (PZV), score, no more than	0.5	0.5	–	0.5	–	0.5	0.5

New additive compositions of M-10G$_2$ oil:

1. M-$11_{Eastern}$ oil, AKI-31, DF-11, C-150, PMC-200A.

2. M-10_{Baku} oil, Viscoplex 2-670, AKI-172 (or AKI-174), DF-11, C-150, Viscoplex 5-309, PMC-200A.

3. M-$11_{Eastern}$ oil, AKI-156d, C-150, DF-11, PMC-200A.

Modifications of synthesized alkylphenolate additives can be used in engine oils for high performance carburetor and diesel engines due to their high quality.

This additive has also been investigated in the composition of M-$14G_2$ engine oil (Table 9).

Ingredients M-$14G_2$: Oil M-14, MASC, HCK, VNIINP-354, PMS-200A. This oil is used in CHN 26/26, CHN 30/38 locomotive and industrial diesel engines.

A new version of the composition of M-$14G_2$ with the additive AKI-156d was developed. As a result of studies of various additives in the additives package, the optimal composition of engine oil M-$14G_2$ was determined in Baku and Eastern oils.

Composition of experimental M-$14G_2$ engine oil:

1. M-12_{Baku} oil, Viscoplex 2-670, AKI-156d, C-150, DF-11, Viscoplex 5-309, PMC-200A.

2. M-$14_{Eastern}$ oil, AKI-156d, C-150, DF-11, PMC-200A.

Table 9 presents the physico-chemical and functional properties of M-$10G_2$ and M-$14G_2$ engine oils.

Studies show that the oil compositions M-8V, M-12VB and M-$10G_2$ fully meet the requirements of GOST and are on the same level with Shell analogues.

With the use of high quality AKI-156d additives in place of the expensive and difficult-to-produce MASC additives, the composition of other additives in the composition is reduced and economically viable by meeting the requirements of engine oil M-$14G_2$.

The proposed additives are distinguished by simple acquisition technology and in small quantities of high quality.

The technical specifications of the AKI-156d additive have been developed and the material balance for the removal of 1 ton of additives has been given. The AKI-156d add-on can be used in all types of engine oils instead of the IXP-101 additive.

Table 9

Comparative test results of M-10G_2 and M-14G_2 oils with high alkaline additives

Names of indicators	M-10G_2 oil			M14G_2 oil			
	GOCT 8581-92 (norma)	con-tain 3	Shell Rimu-la C30	GOCT 8581-92 (norm)	Test oil 1	Test oil 2	M-14G_2 como-dity oil
Kinematic viscosity, 100^0C, mm^2/s	11±0.5	11.3	10.8	13.5-14.5	14.47	14.45	14.5
Viscosity index, no less than	85	93	102	90	90	90	90
Alkaline number. mgKOH/g, no less than	6.0	8.0	9.4	7.0	8.0	8.2	7.2
Sulfate ash,%, no more than	1.65	1.25	1.3	1.3	1.27	1.26	1.28
Flash temperature,^{0}C, Open caste, no more than	205	210	220	210	220	224	210
Freeze temperature, ^{0}C, no more than	Minus 15	Minus 15	Minus 18	Minus 12	Mi-nus 12	Mi-nus 12	Minus 12
Stability of the sedi-mentation induction period (IPO 30 hours), holds	40	40	40	50	50	50	50
Corrosion, (lead plates), q / m^2, no more than	20	None	None	None	None	None	None
Detergent properties, (PZV), score, no more than	1.0	0-0.5	0.5	0.5	0.5	0.5	0.5
Tribological properties (20 ± 5) °C							
Friction factor, kg	–	–	–	34	34	34	34
Crisis load, (P_k) N, not less	–	–	–	823	823	823	823
Diameter of the trace of friction, (D_y) 196N, mm, not more than	–	–	–	0.45	0.45	0.45	0.46

RESULTS

1. As a result of systematic and purposeful research, new qualitative, high-grade, alkylphenolate modifications containing sulfur, nitrogen and various functional groups were obtained. These additives can be used as an alternative to IXP-101, a high ash and low alkaline quantity.

New sulfuric alkylphenolate additives were obtained in an environmentally friendly and efficient manner AKI-144d and AKI-154d [5, 9].

Studies show that AKI-144d based on dodecylphenol is superior to AKI-144 additives based on alkylphenol ($R - C_8 - C_{12}$) with its functional properties and water resistance. This is explained by the fact that low-molecular fat contained in alkylphenol ($R - C_8 - C_{12}$) is poorly soluble and water-washed with 7% butylphenol.

2. By examining the effects of AKI-144d and AKI-144 additives on manometric peroxide radicals, it was found that AKI-144d and AKI-144 additives increase the period of cumulative production and are antioxidants that can prevent oxidation. The AKI-144d additive breaks the peroxide chain more actively and increases the period of cumulus induction compared with the AKI-144 additive, due to its anti-oxidant properties, superior to ionic additives.

3. The alkylphenolate additives that hold the sulfur atom in the side chain of the synthesized and aromatic ring, because of its anti-corrosion properties, the sulfur atom is superior to the alkylphenolate additives in the aromatic rings. It is associated with a steric factor [3, 15, 18].

4. Calcium alkylphenolates were obtained from calcium hydroxide treatment of products derived from the aminomethylating reaction of alkylphenol with various amines and amino acids [1, 2,8].

It has been established that an increase in the number of nitrogen atoms in the amines increases their effects on corrosion, anti-oxidation properties. Thus, AKI-1 additives in nitrogen atoms in 1,2-visinal states are superior to AKI-4 additives at their 1,6-terminal nitrogen atoms [13].

As calcium alkylphenols increase the alkyl radical length of amines, their functional properties deteriorate because of their long-acting alkyl radicals, which reduces its activity [8].

5. In the aminomethylation reaction of amine di (hydroxyalkylbenzyl) with amino acids the ability of amino acid to react is higher than p-aminobenzoic acid. Thus, the reaction with amino acids occurs at 65-75^{0}C and with p-aminobenzoic acid at 85-90^{0}C with the catalyst [16, 29, 30].

Thermo-analytical studies show that the thermal durability of AKI-57 is slightly higher than that of AKI-31.

AKI-31 and AKI-172 additives have been developed in a new way and have been granted patents [30, 31].

6. High-alkaline multifunctional alkylphenolate additives using alkaline calcium alkylphenolates − AKI-154d [9], AKI-156d, AKI-172, AKI-174, etc. were obtained and these additives are superior to their corrosion-resistant properties such as VNIINP-714, OLOA-218A and MASC [4, 11, 21, 23, 31].

7. An effective technology for the production of AKI-156d alkylphenolate additives have been developed, which practically subsitute the high-cost MASC and obsolete alkylphenolate additives without impairing oil expoloitation properties.

The advantage of the developed technology scheme is that it is possible to implement a new additive (AKI-156d) on a existing unit where the alkylphenol additive is produced.

8. It has been established that it is possible to produce engine oils M-8V, M-12V_2, M-10G_2, M-14G_2, which meet modern requirements and have the same level as foreign Shell, with the participation of new multifunctional additives.

The use of high-grade alkaline additives reduces the cost of lubrication composition by simplifying the composition of the additive packages.

The main content of the dissertation has been commented on in the following scientific works

1. Нагиева, Э.А. Диаминосодержащие алкилфенолятные присадки к моторным маслам / Э.А.Нагиева, А.К.Кязим-заде, Х.Н.Мамедьярова, А.А.Гадиров, С.И.Насирова // Азербайджанский химический журнал, − Баку: − 2015. № 2, − с. 67-70
2. Нагиева, Э.А. О влиянии некоторых азотсодержащих алкилфенолятных присадок на качество моторных масел / Э.А.Нагиева, А.К.Кязим-заде, Х.Н.Мамедьярова, А.А.Гадиров, М.Н.Алиева // Азербайджанское нефтяное хозяйство, − Баку: − 2015. № 10, −с.43-45
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