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MULTIFUNCTIONAL ADDITIVE FOR MOTOR OILS ON THE BASIS OF DODECYLPHENOL**E.A.Naghiyeva, A.K.Kazim-zadeh, Kh.N.Mammadyarova, A.A.Gadirov, M.N.Aliyeva, Y.B.Ramazanova***A.Guliyev Institute of Chemistry of Additives, NAS of Azerbaijan**aki05@mail.ru*

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The results on synthesis and research of high alkaline alkylphenolate AKI-134 additive have been introduced. AKI-134 additive is a carbonated calcium salt of the condensation product of dodecylphenol, formaldehyde, ammonia and *p*-aminobenzoic acid. Due to the presence of 2 nitrogen atoms, carboxylate and phenolate groups, the additive shows high anticorrosion, antioxidative and detergent properties. Using AKI-134 additive and commodity additives the M-10Г₂ motor oil has been developed that by their physical-chemical and functional properties meet the standards.

Keywords: dodecylphenol, formaldehyde, ammonia, *p*-aminobenzoic acid, additive, motor oil.

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Introduction

The improvement of the design of internal combustion engines leads to increased demands on the quality of motor oils.

Application of the effective additives is one of the more progressive methods for the quality increase of motor oils.

In composition of modern motor oils as one of the main components a significant part is given to detergent-dispersant additives.

This group of additives includes alkylphenolates, sulphonates and alkylsalicylates. Alkylphenolate additives are found in most modern motor oils. This is due to the availability of raw materials, simple technology of production and multifunctionality of alkylphenolate additives [1–4].

Up to the middle of 1990 in the republics of CIS, most of the alkylphenolate type detergent-dispersant additives produced in industry were barium containing products (BFK, IKhP-101, SIATIM-339 and others). Low alkalinity and high ash content of these additives were the main reason for the reduction or cessation of production of these obsolete additives [5], that didn't meet modern requirements and were inferior to foreign analogues (Амоко-9230, Paranox-51 and others). However they had fulfilled their mission, at that time. By using them, various types of motor oils were developed. In this

regard, there is an urgent need to update the range of alkylphenolate additives and improve their quality.

Analysis of scientific-, technical and patent literature of the last decade showed that of particular interest are high alkaline carbonated alkylphenolates containing metal (most often – calcium).

The most perspective are high alkaline multifunctional additives that in low in small concentrations at the same time improve some properties of lubricating oils [6].

High alkalinity indicates high neutralizing properties of additives [7].

The need in high alkaline multifunctional additives is due to their ability to show high neutralizing and detergent properties in composition of lubricating oils [8].

By introducing various heteroatoms and functional groups into the additive molecules, their antioxidant, anticorrosive and detergent properties are improved [9, 10].

It is known that among metal containing additives for oils alkylsalicylate additives that possess high detergent, thermo-oxidative and other properties have also found wide application. However, in industry they are produced by multi-stage technology, which ultimately complicates the creation of the production technology of this type of additives [11, 12].

Experimental part

In connection with the above, we have proposed a method of obtaining new multifunctional additive for motor oils – AKI-134, which combine simultaneously the properties of alkylphenolate and alkylsalicylate additives.

The process of obtaining the additive includes the following main stages:

- sequential condensation of dodecylphe-

nol with formaldehyde, ammonia and *p*-aminobenzoic acid;

- neutralization of condensation product by calcium hydroxide;
- carbonation of neutralization products and desiccation;
- separation of mechanical impurities by centrifugation.

The estimated formula for AKI-134 additive is:

The additive is a viscous liquid that is of 130–150 mg KOH/g alkaline number.

Following optimal conditions for obtaining additive: dodecylphenol:ammonia:formalin:*p*-aminobenzoic acid:Ca(OH)₂ – 100:(30–35):(40–45):(10–12):(35–40) were established. During carbonation 5% (of alkylphenol) ethylene glycol was used as a promoter. The structure of derived additive has been confirmed by IR spectroscopy that was performed on "Nicolet is 10" spectrometer around 400–4000 cm⁻¹.

In the IR spectrum of the product dodecylphenol condensation with formaldehyde, ammonia and *p*-aminobenzoic acid, bands of absorption of the OH group of the phenolic compound, OH group of *p*-aminobenzoic acid and NH group around 3200–3500 cm⁻¹ were detected.

Valence vibrations of CO groups are registered around $\nu_{\text{C=O}}$ –1716 cm⁻¹ (1690–1760 cm⁻¹), and CN bond around – 1181 cm⁻¹ [13].

After the neutralization of condensation product by calcium hydroxide the 3408 cm⁻¹, stripe appears that is characteristic to valence vibrations of NH group, which was previously covered by OH condensation groups. In the IR spectrum of the neutralization product, the band

of stretching vibrations of the CO of the acid group of 1716 cm⁻¹ disappeared and the corresponding carboxylate of the COO⁻ ions appeared symmetric and asymmetric $\nu_{\text{COO}^-}^{\text{sim}} = 1349$ cm⁻¹ and $\nu_{\text{COO}^-}^{\text{as}} = 1580$ cm⁻¹ instead of it. Regarding calcium hydroxide, in the neutralization product there are absorption bands corresponding to the OH group $\nu_{\text{OH}} = 3670$ cm⁻¹ and CO₃ group of the average intensity band $\nu_{\text{CO}_3^{2-}} = 1430$ and 860 cm⁻¹.

Results and discussion

Physico-chemical and functional properties of AKI-134 additive have been studied in the composition of the M-8 oil using the following standard methods.

Anticorrosive properties were determined according to ГOCT 20502-75, anti-oxidative properties according to ГOCT 11063-77, detergent properties according to ГOCT 5726-2013.

Physico-chemical and functional properties of test additive in composition of M-8 oil are shown in Table 1, where for comparison the data of foreign commodity additives VNIINP-714, OLOA-218A and MASK are also presented.

Table 1. Physico-chemical and functional properties of alkylphenolate additives

Additive	Physico-chemical and functional properties of additives			M-8 oil + 5% additive		
	alkali number, mg KON/g	sulfate ash content, %	kinematic viscosity, at 100°C, mm ² /s	corrosiveness (in lead plates), g/m ²	*stability by induction period of precipitation (IPP 30 h of prec., %)	detergent properties (on PZV), point
AKI-134	145.2	16.1	72.2	1.0	absent	0.5
AKI-134	150.1	16.6	74.8	0.9	absent	0.5
VNIINP-714	143.0	17.2	–	6.4	absent	0.5
OLOA-218A	147.0	17.6	–	9.8	absent	0.5
MASK	140.0	16.8	–	4.5	absent	0.5

*precipitation up to 0.5% is considered absent

Table 2. Physico-chemical and functional properties of M-10Г₂ motor oil

Indicators	ГОСТ 8581-92 (norm)	Test oil M-10Г ₂	Shell oil Rimula C30
Kinematic viscosity at 100°C, mm ² /s	11±0.5	11.45	10.8
Viscosity index, no more than	90	90	102
Alkali number, mg KON/g, no more than	6.0	7.4	9.4
Sulfate ash content, %, no more than	1.65	1.26	1.3
Flash point in open crucible, °C, no lower than	205	205	202
Freezing point, °C, no lower than	minus 15	minus 15	minus 15
Stability by induction period of precipitation (IPP) resistance, h	40	40	40
Corrosion (in lead plates), g/m ² , no more than	20	absent	absent
Detergent properties (on ELV), point	1.0	0.5	0.5

As can be seen on data from Table 1, under the conditions of the tests of test additive AKI-134 on anticorrosion properties surpass comparable industrial analogues, and on antioxidative and detergent properties are on the same level with them.

The improvement of exploitative properties of the additive is apparently related to the mutual influence of 2 nitrogen atoms, carboxylate and phenolate groups on the formation of a stable colloidal dispersion.

Synthesized AKI-134 additive in combination with commodity additives has been studied in the composition of the M-10Г₂ motor oil.

Results of M-10Г₂ oil analysis are shown on Table 2, there are also physico-chemical and functional properties of the foreign analogue – Shell oil.

From data on Table 2, we can see that M-10Г₂ oil with AKI-134 additive meet the requirements of ГОСТ-8581-92 on exploitation properties and is not inferior to the foreign counterpart.

Conclusion

Thus, the possibility of using AKI-134 additive in the composition of M-10Г₂ motor oil as the main component instead of ИХП-101 additive (barium alkylphenolate) is shown.

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MOTOR YAĞLARINA DODESİL FENOL ƏSASINDA ÇOXFUNKSIYALI AŞQAR

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Məqalədə yüksək qələvili AKİ-134 alkilfenolyat aşqarının sintezi və tədqiqi verilmişdir. AKİ-134 aşqarı dodesilfenolun formaldehid, ammoniyak və p-aminobenzoy turşusunun kondensləşmə məhsulunun karbonatlaşmış kalsium duzudur. Aşqar molekulunda iki azot atomu karboksilat və fenolyat qruplarının birgə təsiri sayəsində yüksək korroziyaya, oksidləşməyə qarşı davamlı və yuyuculuq xassələrinə malikdir. AKİ-134 və əmtəə aşqarlarını istifadə etməklə, fiziki-kimyəvi və funksional xassələrinə görə standart normalarına cavab verən M-10Г₂ motor yağı işlənib hazırlanmışdır.

Açar sözlər: dodesilfenol, formaldehid, ammoniyak, p-aminobenzoy turşusu, aşqar, motor yağı.

МНОГОФУНКЦИОНАЛЬНАЯ ПРИСАДКА К МОТОРНЫМ МАСЛАМ НА ОСНОВЕ ДОДЕЦИЛФЕНОЛА

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Приведены результаты по синтезу и исследованию высокощелочной алкилфенолятной присадки АКІ-134. Присадка АКІ-134 представляет собой карбонизированную кальциевую соль продукта конденсации додецилфенола, формальдегида, аммиака и *n*-аминобензойной кислоты. Присадка обладает высокими антикоррозионными, антиокислительными и моющими свойствами благодаря взаимному влиянию 2-х атомов азота, карбоксилатной и фенолятной групп на свойства присадки. С применением присадки АКІ-134 и товарных присадок разработано моторное масло М-10Г₂, которое по своим физико-химическим и функциональным свойствам соответствует стандартам.

Ключевые слова: додецилфенол, формальдегид, аммиак, *n*-аминобензойная кислота, присадка, моторное масло.