Synthetic Sulfonate Additives for Lubricating Oils

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Abstract

Oil-soluble calcium sulfonates on the basis of alkyltetralin obtained using olefins of C20–C30 fraction are developed and characterized. The developed synthetic sulfonate additives with different alkalinity possess high physico-chemical and functional properties and are superior in performance to commercial oil sulfonates C-150 and C-300, as well as foreign analogues – additives OLOA-246B and Hightech 6060M. Using the obtained high-alkaline additive, an experimental motor oil M-10Г2 was developed, which in terms of quality indicators meet the requirments.

Keywords: lubricating oils, alkyltetralin, sulfonate additives, detergent-dispersant additives, motor oils, functional properties.

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Sürtkü yağlarına sintetik sulfonat aşqarları

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Xülasə

Olefinlərin C_{20} - C_{30} fraksiyasından istifadə etməklə alınan alkiltetralin əsasında yağda həll olan kalsium sulfonatları alınmış və xarakterizə edilmişdir. Yaradılmış müxtəlif qələvili sintetik sulfonat aşqarları yüksək fiziki-kimyəvi və funksional xassələrə malik olub, göstəricilərə görə əmtəə neft mənşəli C-150 və C-300 sulfonatlardan, həmçinin xarici analoq olan OLOA -246 B və Xaytek 6060M aşqarlarından üstündürlər. Alınmış yüksək qələvili aşqarın iştirakı ilə keyfiyyət göstəricilərinə görə irəli sürülən tələblərə cavab verən M -10 $Г_2$ tipli təcrübi motor yağı işlənilmişdir.

Açar sözlər: sürtkü yağları, alkiltetralin, sulfonat aşqarları, yuyucu-dispersedici aşqarlar, motor yağları, funksional xassələr.

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Синтетические сульфонатные присадки к смазочным маслам

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Аннотация

Получены и охарактеризованы маслорастворимые сульфонаты кальция на основе алкилтетралина, полученного с использованием олефинов фракции C_{20}-C_{30}. Разработанные синтетические сульфонатные присадки с различной щелочностью обладают высокими физико-химическими и функциональными свойствами и по показателям превосходят товарные нефтяные сульфонаты С-150 и С-300, а также зарубежные аналоги – присадки ОЛОА-246В и Хайтек 6060М. С использованием полученной высокощелочной присадки разработано опытное моторное масло М-1 $0Г_2$, которое по показателям качества отвечает предъявляемым требованиям.

Ключевые слова: смазочные масла, алкилтетралин, сульфонатные присадки, моюще-диспергирующие присадки, моторные масла, функциональные свойства.

Introduction

Presently in the refining industry of the developed countries of the world the most important place is given to increasing the production of high-quality motor oils that meet the requirements of modern and advanced equipment at the expense of the wider application of effective additives for various purposes, including sulfonates. High alkaline sulfonates derived on the basis of petrol oils and synthetic alkyl aromatic carbohydrates in relatively small concentrations provides motor oils with high detergent-dispersant properties [1-3]. It is becoming important to investigate the production of synthetic sulfonates, which have a number of advantage over petroleum sulfonates: higher content of active substance, relative simplicity of production technology, and better functional and service properties [4,5]. In addition, in the production of petroleum sulfonates, a significant amount of hardly utilizable waste is formed - acid tar (up to 30%).

Purpose of work – Expanding the raw material base for the production of synthetic sulfonate additives and increasing the efficiency of their action.

The solution of the problem – We have carried out the synthesis of detergent-dispersant sulfonate type additives on the basis of alkyltetralin were obtained using propylene oligomers, and their effect on the properties of lubricating oils has been studied.

The initial alkyltetralin was obtained by alkylation of tetralin with olefins of C_{20}–C_{30} fraction in the presence of a zeolite-containing catalyst according to method [6] under conditions that ensure the highest yield of monoalkyl derivative. As a result alkyltetralin with 82% yield was synthesized with following physico-chemical parameters: density at 20 ^{0}C – 916.3 kg/m3; index of refraction n_D^{20}– 1.5190; molecular mass–480; boiling point, ^{0}C – > 430 ^{0}C.

The sulfonation of alkyltetralin was carried out with sulfur trioxide gaze at a molar ratio of 1:1.2 in an octane solution at a temperature of 40–45 ^{0}C for 2 hours. In the product of sulfonation, the mass fraction of oil-soluble sulfonic acids is 79%.

Neutralization of alkyltetralinsulfonic acids was carried out with an aqueous suspension of calcium hydroxide at a temperature of 70–75 ^{0}C for 3 hours till the weakly alkaline reaction, after the temperature was raised to 125–130 ^{0}C for evaporation reaction water. The resulting product was dissolved in octane, mechanical impurities were separated by centrifugation and the solvent was distilled off.

Carbonation of neutral sulfonate with carbon dioxide in the presence of excess calcium hydroxide, promoter – methanol, oil diluents M-6, solvent – toluene at a temperature of 40–45 ^{0}C for 1 hour were produced medium-alkaline (C-150 type) and high-alkaline (C-300 type) additives.

Composition and structure of the sulfonates were confirmed by elemental analysis and IR spectroscopy. The calcium content was determined on a metal analyzer MP-4200 AES, IR spectra were taken from on a spectrometer NICOLET IS-10. Content of active substance in additives was determined by method liquid adsorption microchromotography.

In the IR spectra of the sulfonates there are absorption bands in the regions of 1050–1070 and 1160–1250 cm^{-1} resulting from valence symmetric and asymmetric vibrations of the S=O bonds of the SO_3 group. The most

characteristic of the spectra of alkaline sulfonates is the presence of bands in the region of 850–880 and 1400–1500 cm^{-1} related to vibrations of the carbonate of the CO_3^{-2} ion.

The studies of the physico-chemical and functional properties of additives were carried out by standard laboratory methods [7]. The detergent properties were determined on a PZV unit accordance with GOST 5726–2013, dispersion properties at 250 ^{0}C, according to the technique described in [8]. The anticorrosive properties were evaluated on a DK-NAMI device at 140 ^{0}C for 25 hours, according to GOST 20502-75, the oxidation stability was measured on a DK-NAMI device for 30 hours at 200 ^{0}C according to GOST 11063-77.

Colloidal stability of the dispersions was evaluated by decomposing the additive with 15% of distilled water at 110 ^{0}C for 4 hours and precipitating with benzene followed by centrifuging [9]. Stability of colloidal dispersion was established on a decrease of alkalinity of the additive expressed in percentage of the initial one.

The thermal stability of additives was studied with derivatograph of the OD-102 T type of the Paulik system (Hungary) in a dynamic heating mode at a speed of 5 C/min in air. The standard was calcined aluminium oxide.

The obtained additives NSK_{at} (neutral), $CC\text{-}150_{at}$ (medium-alkaline) and $CC\text{-}300_{at}$ (high alkaline) are viscous liquids of dark brown color, the characteristics of which are shown in Table 1 and 2. In the same place for comparison are presented similar indicators of commercial petroleum sulfonates C-150 and C-300, as well as foreign analogues – additives OLOA 246B and Hightech 6060M.

Synthesized additives have a micellar structure characteristic for sulfonates. They have high physico-chemical and functional properties. With the introduction of the developed additives in the oil M-11 at a concentration of 5%, its detergent, dispersant, neutralizing, anticorrosive properties and stability against oxidation are significantly improved.

Table 1 – Characteristics of neutral sulfonate additives

Indicators	Neutral sulfonates	
	NSK_{at}	OLOA 246 B
Alkaline number, mg KOH/g	28	23
Mass fraction, %, of calcium sulfonate calcium mechanical impurities	 80.5 6.3 0.06	 41.1 - 0.1
Sulfat ash, mass. %	11.2	8.6
Detergent properties on installation PZV, points*	0	0.5
Dispersant ability at 250 ^{0}C, %*	50	40

*M-11 oil with 5% additive

Neutral alkyltetralin sulfonate has a higher content of the active substance, a lower content of mechanical impurities and better dispersant properties as compared to the OLOA 246B additive.

By their detergent properties the synthesized medium- and high-alkaline additives are on the same level with product additives such as C-150 and C-300 additives, and surpass them in dispersant, anticorrosion properties and stability against oxidation. Thus, the dispersant properties of the additives CC-150_{at} and CC-300_{at} are 70 and 80%, respectively, while for the additives C-150 and C-300, these indices are equal to 60 and 75%. In addition, experimental additives have a higher stability of the colloidal dispersion to the action of water than theiranalogs.

The alkaline sulfonates developed by a number of indicators are superior to their foreignanalogs. Thus, the growth in viscosity of the oxidized oil in the presence of additives CC-150_{at}, CC-300_{at} and Hightech 6060M is 62, 54 and 78%, respectively.

The data obtained are consistent with the results of thermoanalytical studies of additives. The developed sulfonates are characterized by high thermal stability and are superior to their foreign analogue in this parameter. Thus, the temperature at which the weight loss of additives, NSK_{at}, CC-150_{at} and CC-300_{at} is 50%, reaches 410, 420 and 435 ^{0}C, respectively, against 400 ^{0}C.

Table 2 – Characteristics of medium- and high alkaline sulfonate additives

Indicators	Medium and high alkaline sulfonate additives				
	CC-150_{at}	C-150	CC-300_{at}	C-300	Hightech 6060M
Alkaline number, mg KOH/g	156	150	307	303	142
Mass fraction of calcium sulfonate, %	32.4	31.5	32.3	30.0	32
Mass fraction of calcium, %	13.8	13.4	27.7	26.9	-
Sulfate ash, mas. %	24	23.0	44.4	42.9	23.1
Mass fraction of mechanical impurities,%	0.04	0.08	0.04	0.09	0.05
Temperature of flashes in open in crucible, ^{0}C	190	180	210	200	185
Detergent properties on installation PZV, points *	0	0	0	0	0.5
Dispersant ability at 250 ^{0}C, % *	70	60	80	75	60
Corrozion of lead plates, g/m^2 *	73	85	60	90	85
Stability over the induction period of precipitation: sludge, % increase in viscosity, %	 0.5 60	 0.7 71	 0.4 49	 0.8 77	 0.9 78
Colloidal dispersion stability, %	88	75	99	90	76

*M-11 oils with 5% additive

Table 3 – Characteristics of experimental motor oil M-10G_2 for the Hightech 6060M additive.

Indicators	M-10G_2 motor oil		
	GOST 8581-92	experimental	Shell Rimula C 30
Kinematic viscosity at 100 ^{0}C, mm^2/s	11 ± 0.5	11.2	10.8
Viscosity index, not less than	85	90	102
Sulfat ash, %, no more than	1.65	1.43	1.3
Alkaline number, mg KOH to 1g oil, no less than	6.0	8.4	9.4
Temperature, ^{0}C, of: flashes in open crucible, no less than hardening, no higher than	 205 - 15	 205 - 15	 202 -15
Detergent properties on installation PZV, points, no more than	1.0	0	0.5
Stability over the induction period of precipitation, h, no less than	40	40	40
Corrozion of lead plates, g/m^2, no more than	20	none	none

Using the most effective high-alkaline additive CC-300$_{at}$, has been studied as a detergent-dispersant component in combination with antioxidant and anticorrosion additives in the lubricating composition of M-10G_2 motor oil intended for automotive diesel engines.

The results of laboratory tests (Table 3) showed that the use of the synthesized sulfonate ensures the production of test oil M-10G_2 with nigh physico-chemical and functional (detergent-dispersant, antioxidant, anticorrosive) properties corresponding to the requirements imposed on these oils. The developed oil in its performance is not inferior to the foreign analogue - the oil of the M-10 G_2 type of the Shell company.

Conclusion

Based on the product of tetralin alkylation, propylene oligomers of the C18–C30 fraction were used to synthesize neutral, medium- and high alkaline oil-soluble calcium sulfonates, which significantly improve the functional properties of lubricating oils, and also have a high stability of colloidal dispersion to water action.

High efficiency of the developed additives allows them to be used as a detergent-dispersant component in the composition of additive packages for modern motor oil.

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