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DEVELOPMENT OF SYNTHESIS CONDITIONS OF NEUTRAL CALCIUM SULFONATE DILUTED IN SYNTHETIC OILS

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Abstract:
In the paper, the possibility of synthesizing neutral calcium sulfonate based on synthetic long-chain linear alkylbenzene sulfonic acid (LLABSA) is investigated. The aim of this work was to synthesize an additive that is highly soluble in API group I, III and IV base oils, with a high level of physico-chemical properties, using a mixture of base oil and ester as the diluent oil. As a result, a neutral calcium sulfonate was obtained, and its influence on the specific properties of oils I, III, and IV of the API Group at a 2% concentration was studied. The composition and structure of the obtained sulfonates were investigated using inductively coupled plasma atomic emission spectrometry (ICP-AES) and infrared spectroscopy (FTIR) methods. The obtained calcium sulfonate is not inferior to the commercial additive NSCS-30 produced by "AddiTech" in terms of detergent-dispersing, anti-wear and anti-corrosion properties.

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1. INTRODUCTION

Lubricating oils play an important role in the operation of various mechanisms and equipment in industrial processes, ensuring their reliable and long-lasting operation. Proper use of lubricants increases the life-time and efficiency of equipment and reduces the long-term costs of energy consumption and maintenance needs and lowers operating temperatures [1,2].

The primary function of a lubricant is to create a film barrier between moving mechanical parts, thereby reducing friction and wear. It also acts as a coolant, inhibiting the formation of harmful deposits and controlling corrosion and oxidation processes. Since base oil alone cannot meet these complex requirements, additives are added to the oil to enhance the material's performance [3].

The share of motor oil production in the lubricants market is approximately 60%, with up to 5% of the total comprising detergent-dispersant additives [4]. Detergent-dispersant additives make up the main part (45-50%) of all produced additives to oils, as they are the main component of additives' packages for engine, gear oils and tractor hydraulic system working fluids – all those products that are produced in significant volumes [5,6].

At the same time, promising additives are known, such as ionic liquids used as multifunctional additives in lubricating oils [7-9].

Detergent additives prevent the formation of deposits on metal surfaces of machinery parts and limit corrosion processes due to their surface activity. The most common such additives are calcium and magnesium sulfonates [10-12].

The synthesis of neutral calcium sulfonates is carried out by neutralization of linear alkylbenzene sulfonic acids, which can contain in their structure both one and two alkyl radicals of different molecular weights [5,13]. The length and branching of the hydrocarbon radical have a fundamental influence on oil solubility and detergent properties. For the synthesis of calcium sulfonates, it is preferable to use alkylbenzene sulfonic acids with one weakly branched radical C_{24} (Long-chain Linear Alkylbenzenesulfonic Acid – LABSA), or with two

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linear radicals C_{12} (dialkylbenzene sulfonic acid – DABSA) [10,14].

Neutralization of linear alkylbenzene sulfonic acid with calcium hydroxide in a mixture with oil in a hydrocarbon solvent is carried out in industrial processes according to the scheme shown in Figs. 1 and 2, with possible formation of neutral (Fig. 1) and based (Fig. 2) calcium sulfonate.

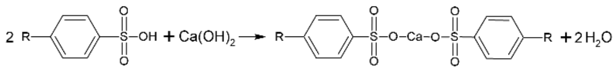

Fig. 1. Reaction of neutral calcium sulfonate formation

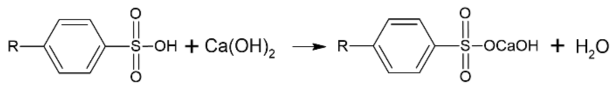

Fig. 2. Reaction of based calcium sulfonate formation

The promoters of the neutralization reaction are acetic acid, alcohol or water, which are introduced into the reaction mixture to intensify the reaction of inorganic calcium hydroxide with organic alkylbenzene sulfonic acid [15-17]. There is no universal promoter; the suitable one in each case has to be selected experimentally. The temperature of the neutralization stage strongly depends on the raw materials used, solvent, promoter, diluent oils and several other factors [5].

The main engine tests for evaluating the detergent-dispersant properties of engine oils containing detergent additives are Sequence III (ASTM D7320) and Sequence V (ASTM D6593). The modern requirements of API SP and API CK-4 specifications force lubricants manufacturers to completely abandon petroleum origin lubricants. The same is required in additive manufacturing processes - petroleum sulfonates dissolved in petroleum oils do not allow the creation of effective motor packages capable of providing the required level of performance properties [18,19]. Thus, the task of obtaining synthetic calcium sulfonates stabilized in solution in oils of groups API III, IV and V is relevant [20-22].

2. MATERIALS AND METHODS

In the laboratory of functional additives for lubricants at Gubkin University, 11 samples of neutral calcium sulfonate with different component ratios in diluent oil were obtained. The synthesis was carried out according to a single technique developed in the laboratory. For all obtained additive samples, the basic physico-chemical properties were determined and compared with the commercial additive. The most successful sample of the synthesized additive was introduced into API group I, III and IV oils at a concentration of 2% by weight. Anti-wear and anti-corrosion properties, as well as the effect on high-temperature oxidation were determined.

Isoparaffin oil and DOTP ester (Dioctyl terephthalate) were used as components of the diluent oil. Different compositions of diluent oil are given in Table 1.

Table 1. Diluent oil compositions

Number	VHVI-4, %weight	DOTP, %weight
1	100	0
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50
7	40	60
8	30	70
9	20	80
10	10	90
11	0	100

LABSA produced by “NORKEM“ was used for synthesis. The results of the determination of its physicochemical properties are given in Table 2.

Table 2. Physicochemical properties of “NORKEM“ LABSA

Parameter	**Technical specifications 20.41.20-015-71150986-2023**	**Value**
Active matter content, %	> 77	79,3
Sulfuric acid content, %	< 0,4	0,31
Total Acid Number – TAN, mg KOH/g	90-100	97,2
Color of 1% ethanol solution, ASTM color scale	< 3	1,9
Molecular weight of active matter, g/mole	-	478

As mentioned earlier, a mixture of VHVI-4 hydroisomerization oil and synthetic ester DOTP was used as a diluent oil. To reduce the viscosity of the reaction mass, toluene was used as the solvent. Water was used as a promoter of the neutralization reaction. The material balance of synthesis is given in Table 3.

Table 3. Material balance of synthesis

Component	Mass, g	%weight
LABSA*	42	21
Diluent oil	54	27
Toluene	74	37
Calcium hydroxide**	6	3
Water	24	12
Summary	200	100

Note:
* The acid concentration is determined by the expected active matter content in the resulting additive (40-50%).
** An equimolar ratio of calcium hydroxide was taken to obtain the possibility of synthesizing based calcium sulfonate in order to change the additive's TBN.

The synthesis was carried out according to the following procedure:

- A solution of sulfonic acid in diluent oils and solvent was prepared.
- A suspension of calcium hydroxide and water was added under constant stirring.
- The mixture was kept at a specific temperature (temperature regimes in the range of 40-80°C with a step of 10°C were investigated) for 2 hours.
- The reaction mass was centrifuged for 15 minutes at 3500 rpm.
- The fugate was subjected to thermal stabilization at 120°C at a residual pressure of 0.1 bar for 4 hours to remove water and solvent [23,24].

Identification of the obtained products was carried out according to the following methods:

- Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids, ASTM D445.
- Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester, ASTM D92.
- Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation, ASTM D95.
- Standard Test Method for Particulate Contamination in Middle Distillate Fuels by Laboratory Filtration, ASTM D6217.
- Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration, ASTM D664.
- Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration, ASTM D2896.
- Standard Test Method for Refractive Index and Refractive Dispersion of Hydrocarbon Liquids, ASTM D1218.
- Standard Practice for Condition Monitoring of In-Service Lubricants by Trend Analysis Using Fourier Transform Infrared (FT-IR) Spectrometry, ASTM E2412.
- Standard Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), ASTM D5185.
- Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry, ASTM D4294.
- Content of active matter (calcium sulfonate) by the two-phase titration method, developer's method.

The possibility of using the synthesized additive as an anti-wear, anti-corrosion and detergent-dispersant additive according to the methods was evaluated:

- Standard Test Method for Wear Preventive Characteristics of Lubricating Fluid (Four-Ball Method), ASTM D4172.
- Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test, ASTM D130.
- High temperature catalytic oxidation on G.Y. Shore's tester (HTCO, explanation below).

A five-spindle installation was used in the present work to simulate the ageing of engine oil under operating conditions. One of its details is shown in Fig. 3.

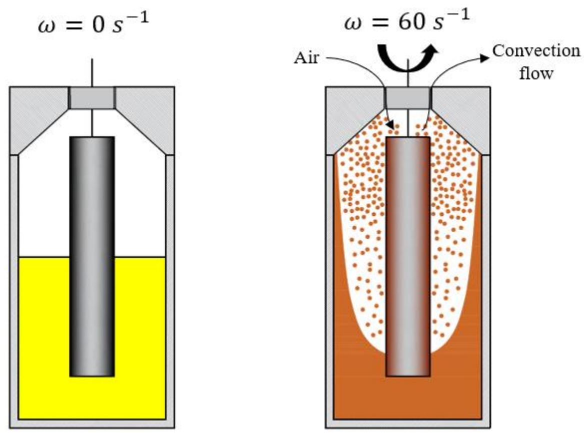

Fig. 3. HTCO test

The rotating rods are placed coaxially in a fixed heated cup. In the engine, the distance between the cylinder and the piston is minimal, and the engine oil is subjected in this area to maximum thermomechanical and oxidation stress in the force field between galvanocouples of different metals, acting as catalysts for high-temperature transformations of oil hydrocarbons within the engine. This is especially important for understanding the mechanism of piston high-temperature deposit formation.

3. RESULTS AND DISCUSSION

The influence of the diluent oil composition on the homogeneity of the resulting additive (synthesis was carried out at 60°C) is shown in Fig. 4. The solubility of the synthesized additives (flakes formation) was assessed by introducing 5% by weight of all 11 additive samples containing various amounts of ester into VHVI-4 base oil. As can be seen from Fig. 4, some additives dissolve only at temperatures of 30°C and above. At the same time, samples containing 10-70% of the ester dissolve well already at room temperature. Therefore, they were cooled to -30°C in order to determine the temperature of flocculation. As shown in Fig. 4, a sample containing 30% by weight of ether is the most stable over the entire temperature range.

Since calcium sulfonate is a highly polar substance, its stabilization in non-polar oil VHVI-4 is challenging. DOTP is a polar aromatic ester with high solubilizing power. With an increasing concentration of DOTP in the diluent oil, the colloid stability of the calcium sulfonate increases, making the additive homogeneous even at low temperatures. When the DOTP concentration exceeds 30%, the opposite effect is observed. This is due to the phenomenon of hydrolysis, which actively proceeds during the distillation of water and solvent in the presence of residual sulfonic acid and water. Hydrolytic destruction of DOTP molecules leads to the release of 2-ethylhexyl alcohol and terephthalic acid insoluble in oil.

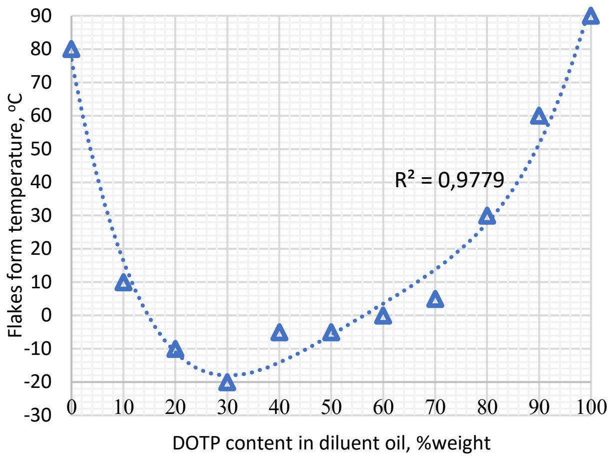

Fig. 4. Effect of DOTP contamination on structure formation in the additive

For further studies, a diluent oil consisting of 30% DOTP and 70% VHVI-4 was used. The results of synthesis at different temperatures are shown in Table 4. The target values of the parameters are taken based on the analysis of the Technical Conditions for the production of similar commercial additives.

Table 4. Results of comparative analysis of synthesized products

Parameter	Target	40°C	50°C	60°C	70°C	80°C	90°C
TAN, mg KOH/g	< 5	21.3	7.2	3.5	3.8	3.6	3.5
TBN, mg KOH/g	< 40	2.1	5.4	13.2	28.1	42.4	48.2
Refractive index of Sodium D-line at 20°C	-	1.4781	1.4788	1.4791	1.4793	1.4795	1.4796
Sulfur content, %	-	2.25	2.30	2.32	2.29	2.26	2.30
Calcium content, %	2 - 2,5	0.77	1.01	1.87	2.31	2.72	3.08
Water content, %	< 0,2	0.12	0.15	0.15	0.12	0.16	0.14
Kinematic viscosity at 100°C, cSt	< 50	18.41	19.82	27.42	42.12	65.19	86.24
Flash point, °C	> 200	232	230	228	234	230	232
Particle contamination, %	< 0,10	0.05	0.05	0.06	0.08	0.17	0.21
Calcium sulfonate content, %weight	40-45	17	33	42	43	42	43

Based on the data in Table 4, the following conclusions can be drawn:

1) At temperatures below 40°C the reaction rate is low (characterized by a high residual acid number after 2 hours of synthesis), so the process will take considerable time, which will deteriorate the economics of production.

The residual acid number is an excellent indicator of the completeness of the neutralization reaction of the organic sulfonic acids. The reaction process was also monitored by FTIR spectroscopy. FTIR spectra of the solution of the initial sulfonic acid in diluent oil and the obtained additive are shown in Fig. 5.

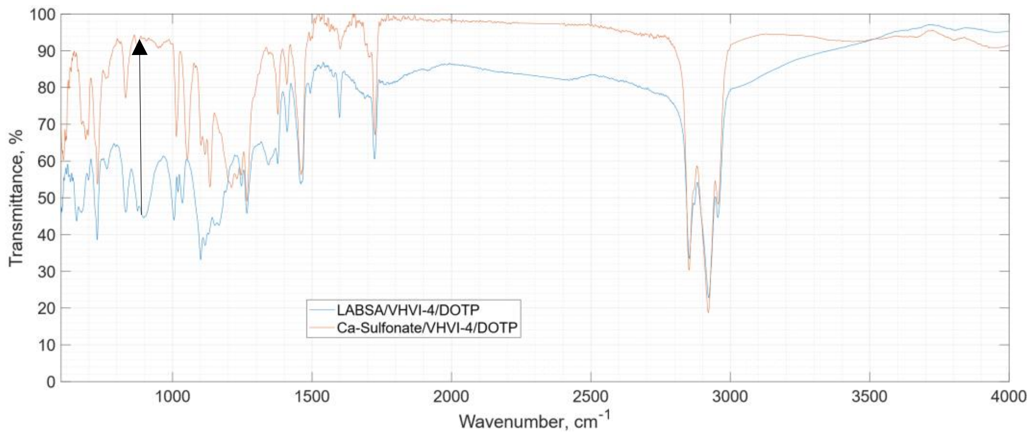

Fig. 5. FTIR-spectra of LABSA/Diluent and Ca-sulfonate/Diluent compounds (*Note: The black arrow indicates the absence of O-H bending vibrations after synthesis, which characterizes the completeness of neutralization*)

The O–H out-of-plane bending vibrations were observed at 909 cm^{-1}; their disappearance during synthesis characterizes the completeness of neutralization. The stretching modes of the sulfonic acid functional group $-SO_3H$ occurred in the region of 1200-1000 cm^{-1}: The asymmetric stretching vibrations of sulfonic group occurred at 1177 cm^{-1} and the symmetric stretching vibrations of the sulfonic group occurred at 1035 cm^{-1}, 1007 cm^{-1}. During the transformation process of the sulfonic acid group to the $-SO_3Ca$ group, a slight shift of the indicated peaks toward high frequencies is observed [25-28].

2) At temperatures above 70°C, active formation of based calcium sulfonate began in the presence of an excessive amount of calcium hydroxide, resulting in a significant increase in viscosity, TBN and calcium content (Figs. 6 and 7).

3) As the TBN of sulfonate increases, its viscosity increased significantly and the centrifugation process became more complicated (the residual calcium hydroxide particle contamination in additives obtained at 80°C and 90°C did not meet the requirements). This leads to the necessity of involving large amounts of supplementary solvent for centrifugation.

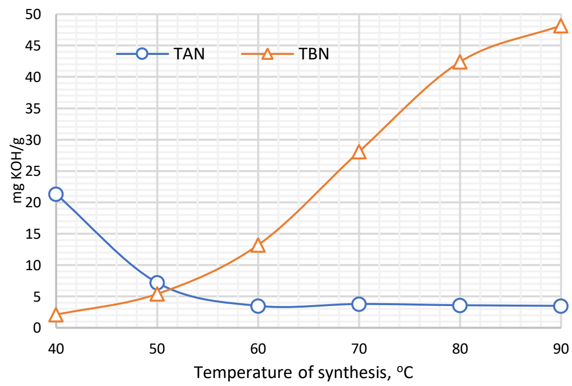

Fig. 6. Dependence of TAN/TBN on synthesis temperature

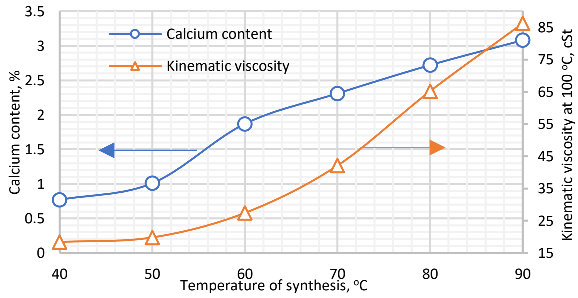

Fig. 7. Dependence of calcium content and additive viscosity on synthesis temperature

Table 5 shows the comparison of physical and chemical properties of the synthesized additive in the optimal conditions and the commercial additive named NSCS-30 produced by "AddiTech".

Table 5. Physical and chemical properties of commercial and synthesized additives

Parameter	Commercial additive (NSCS-30)	Synthesized additive (SA)
TAN, mg KOH/g	1.2	3.8
TBN, mg KOH/g	15.5	28.1
Refractive index of Sodium D-line at 20 °C	1.4911	1.4793
Sulfur content, %	2.86	2.29
Calcium content, %	2.32	2.31
Water content, %	0.12	0.12
Kinematic viscosity at 100°C, cSt	25.95	42.12
Flash point, °C	230	234
Particle contamination, %	0.09	0.08
Calcium sulfonate content, %	45	43

IR spectra of the commercial and synthesized additives are shown at Fig. 8.

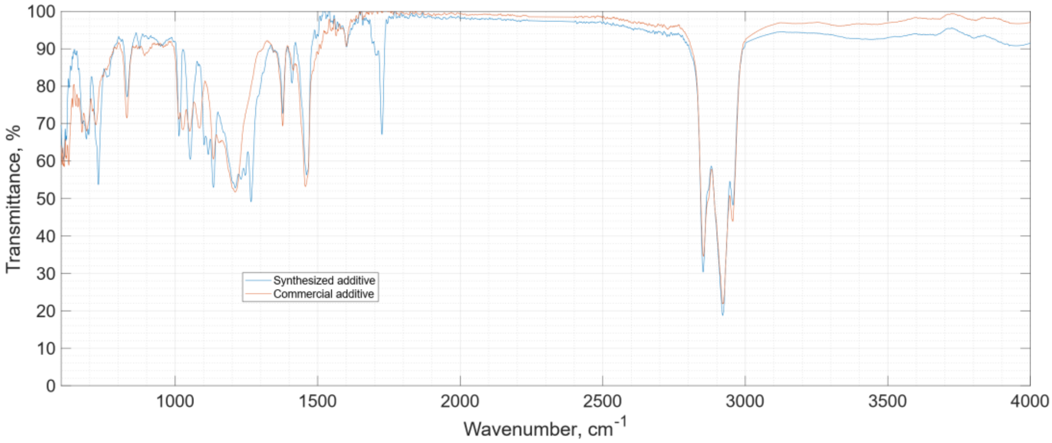

Fig. 8. FTIR-spectra of commercial and synthesized additives

The C–H stretching vibrations for methyl and methylene are the most characteristic in terms of organic compound containing long aliphatic chain. The stretching modes of methyl and methylene groups occurred in the 3000-2800 cm^{-1} region. The C–H asymmetric/symmetric stretching vibrations of methyl group occurred at 2959 cm^{-1}, 2872 cm^{-1} and the C–H asymmetric/symmetric stretching vibrations of methylene groups occurred at 2922 cm^{-1}, 2853 cm^{-1}. Two peaks at 1465 and 1377 cm^{-1} are assigned to the C–H bending vibrations of methylene as well as to the methyl group [25]. The characteristic absorption peaks of the benzene ring are observed: C–C stretching vibrations of the benzene ring appeared at 1601 and 1495 cm^{-1} [25]. The long carbon chain out-of-plane bending vibration was at 728 cm^{-1}. The stretching modes of the sulfonic functional group -SO_3Ca occurred in the regions of 1000-1200 cm^{-1}, 1010-1080 cm^{-1}. There were no 900 cm^{-1} vibrations of the -OH group in sulfonic acids.

The peculiarity of the synthesized additive is the peak at 1720 cm^{-1}, which appears due to the bending vibrations of the carbonyl group in DOTP. In general, the spectral pattern of the additives is similar but not identical, this is explained by the fundamentally different chemical composition of the used diluent oils. The commercial additive is obtained using a petroleum diluent oil consisting of a wide range of different hydrocarbons, including hybrid structure matters, as well as heteroatomic compounds. Therefore, a fully matched additive spectrum in the fingerprint region 1300-650 cm^{-1} is not possible.

The results of the investigation of the effect of synthesized additive (SA) on anti-wear properties of API group I, III and IV base oils are presented in Table 6.

Additive synthesized in optimal mode enhances the anti-wear properties of API group I, III and IV oils. The best effect is shown in VHVI and PAO oils. The injectivity concerning anti-wear properties in SN-150 oil is worse due to heteroatomic compounds contained in petroleum oil, which tend to enter into competitive adsorption with the additive. The level of anti-wear characteristics of SA and NSCS-30 additives is similar.

Table 6. Anti-wear properties of base oils with an additive

Composition	Kinematic viscosity at 40 °C, cSt	Four ball wear scar, 196 N, 60 min
VHVI-6	32.12	0.66
VHVI-6 + 2% NSCS-30	33.25	0.42
VHVI-6 + 2% SA	33.38	0.43
PAO-6	31.12	0.71
PAO -6 + 2% NSCS -30	32.02	0.41
PAO -6 + 2% SA	32.51	0.40
SN-150	30.86	0.59
SN-150 + 2% NSCS -30	31.22	0.52
SN-150 + 2% SA	31.34	0.50

The study of the anticorrosive action of the obtained additive on copper was carried out. The results are given in Table 7.

Table 7. Anticorrosive properties of base oils with additive

Composition	Sulfur content, %	Copper corrosion degree, 120°C, 3 hours
SN-150	0.08	3a
SN-150 + 2% NSCS-30	0.14	1b
SN-150 + 2% SA	0.13	1b
SN-150 + 3% EP-Additive	0.83	4a
SN-150 + 3% EP-Additive + 2% NSCS-30	0.90	2d
SN-150 + 3% EP-Additive + 2% SA	0.89	2d

The obtained neutral calcium sulfonate reduces the intensity of chemical corrosion of the copper. This effect is especially expressed in oil containing active sulfur from the extreme-pressure additive. Before the addition of calcium sulfonates, a transparent black layer of copper sulfide was formed on the copper plate. After the addition of SA, only moderate tarnish was observed.

The detergent properties of oils with additives were evaluated on a five-spindle HTCO (high-temperature catalytic oxidation) tester under the following conditions:

- Aluminum rod and steel cup were first cleaned to a shine and wiped with gasoline.
- Five steel beakers were filled with 20 ml of test oil each.
- Beakers containing oil were inserted into the cells of the enclosure and heated to 230°C.
- When the set temperature value was reached, the rotation unit was lowered and the rod rotation drive was switched on.
- The oil was oxidized for 180 minutes at 230°C.
- At the end of oxidation, oil samples were taken for analysis, and the mass of deposits on the rod after solvent washing and drying was determined.

The HTCO tester simulates oil ageing in the most heat-stressed part of the combustion engine – the piston ring zone.

M-11 petroleum oil (mixture of SN-150, SN-400 and BS oils) was taken as the oil under study. As a promoter of deposit formation, 1% by weight of finely dispersed carbon (soot), with a dispersity of 1-10 µm was added to the oil. The test results are presented in Table 8.

Table 8. Detergent properties of oils

Composition	TAN, mg KOH/g		Sum of rods deposits, mg
	Before oxidation	After oxidation	
M-11 + 1% soot	0.15	16.2	50.9
M-11 + 1% soot + 2% NSCS-30	0.18	8.2	16.9
M-11 + 1% soot + 2% SA	0.17	5.4	13.7

The developed additive has no effect on oxidative stability of oil, but prevents formation of high-temperature deposits in the presence of soot, and also promotes neutralization of acidic products of oxidative degradation. This is confirmed by the decrease in the mass of deposits at the HTCO test, as well as by the decrease in the acid number of oxidized oils.

4. CONCLUSION

Based on the results of the study, the following conclusions can be drawn:

- A neutral calcium sulfonate was obtained in a solution of synthetic diluent oils.
- The optimum technological mode of synthesis of neutral calcium sulfonate, under which conditions it is possible to obtain an additive with the required physical and chemical parameters, has been selected.
- The possibility of using an ester of terephthalic acid and 2-ethylhexyl alcohol as a component of diluent oil has been shown.
- The synthesized additive is well soluble in API group I, III and IV oils within a concentration range of up to 2%.
- The possibility of using the obtained compound as an anti-wear, anti-corrosion and detergent additive to lubricants has been shown. The efficiency of the obtained additive is comparable to the commercial product NSCS-30 produced by "AddiTech".

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Conflicts of Interest

The authors declare no conflict of interest.

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