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INFLUENCE OF CARBOXYLIC ACIDS ON FILTERABILITY AND QUALITY LEVEL OF SYNTHETIC LOW ALKALINE CALCIUM SULFONATE (DETERGENT-DISPERSANT MOTOR OIL ADDITIVE)

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The study examined the conditions of synthetic low alkaline calcium sulfonate (SLCS) synthesis, which is added to motor oils as a detergent-dispersant additive. In particular, the effect of the introduction of carboxylic acids at the stage of SLCS synthesis on such characteristics of the additive as the observable filterability, volume filtration rate, volume fraction of sediment and kinematic viscosity was studied. For the obtained additive samples the average sizes of particles dispersed in the volume were measured using the dynamic light scattering method (DLS) and the basic physicochemical parameters were determined.

Keywords: *detergent-dispersant oil additives, lubricants, filterable sulfonate additives, calcium sulfonate.*

Introduction. This article discusses the preparation of synthetic low-alkaline calcium sulfonate (total base number< 50 mg KOH/g) based on high molecular weight sulfonic acid (dialkylbenzenesulfonic acid (DABSA)) as a detergent-dispersant additive to motor oils. Synthesis of low alkaline sulfonates using synthetic high molecular weight sulfonic acids (synthetic acids of average molecular weight 450 Da or more) is associated with certain problems. Calcium salts of high molecular weight sulfonic acids are viscous materials prone to the formation of supramolecular complexes with irregular structure. This creates certain problems in the process of their synthesis and then utilization. Moreover, it is possible that calcium hydroxide particles can be included in the formed aggregates during the synthesis process. This kind of dispersed system can be classified as filled concentrated, in which interactions between existing supramolecular formations are possible. So, this leads to the enlargement of the latter. The dispersed system in this case is thermodynamically and kinetically unstable due to aggregation and subsequent sedimentation of the existing particles. Inability to resist aggregation leads to coagulation of sol particles of calcium hydroxide with their subsequent coalescence (irreversible fusion), which leads to sedimentation as a result. Moreover, the aggregation of sol particles can lead to the formation of a macrophase of calcium hydroxide or to the transition of the sol into a gel in the case of presence of a surfactant. Furthermore, by rheological properties such structures can be considered as dilatants, i.e. they tend to increase their viscosity with an increase in shear deformations. This fact complicates filtration or makes it completely impossible. Thus, in order to create calcium sulfonates stable in quality level, it is necessary to increase somehow their ability to resist aggregation.

There are methods of producing sulfonates with a low alkaline number in which carboxylic acids are used [1]. It is expected that carboxylic acids prevent the formation of gel-like products, reduce the viscosity of the obtained additive and reduce the amount of sediment. As a result, this provides fluid, filterable products. This effect is probably a consequence of the interaction of carboxylic acid with the fractions of calcium hydroxide particles of the size lying in the region of tens of nanometers. Such particles have a large free energy reserve and therefore easily undergo various transformations. This allows their selective removal. Also, particles of such sizes are presumptively able to clog the pores of the filter, and this also complicates the filtering process.

The purpose of this study is to synthesize SLCS with acceptable filterability. To accomplish this task acetic acid is added at the stage of additive synthesis. Acetic acid reacts with the excess base to form an acetate which can be dispersed in the sulfonate soap media in the product.

Experiment

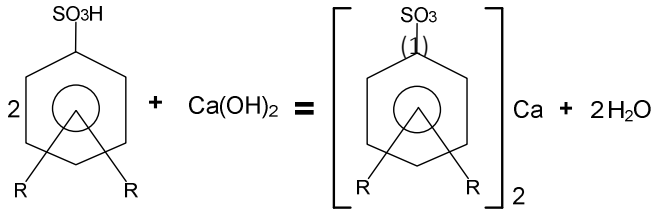
Reagents. Using the previous studies on the selection of raw materials for the synthesis of low alkaline calcium sulfonate and results received by JVLL "LLK-NAFTAN", high molecular weight DABSA (M = 460 g /mol) with an active component content of 84% by mass was selected. The spindle oil SN-150, calcium hydroxide, technical toluene, technical acetic acid "analytical grade", distilled water satisfy all quality requirements. At the filtration stage of the obtained product, Celite-545 diatomaceous earth was used.

Apparatus. For the neutralization reaction, a three-necked flask connected to a mixer, a thermometer and a backward cooler was used. A water bath was used to control the temperature in the reactor. A rotary evaporator was used to remove toluene and water. A Malvern Zetasizer Nano ZS DLS spectrometer was used to determine the average particle sizes.

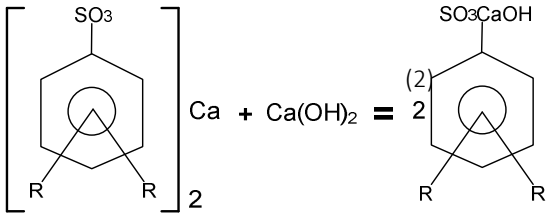
Tests. The average molecular weight of the DABSA was determined in accordance with ASTM D-3712. The ASTM D-664 test was used to determine the total acid number. The total base number of products was determined potentiometrically in accordance with ASTM D4739-17.

Procedures. The reactions occurring during the synthesis are described by the following chemical equations:

1) Preparation of neutral calcium sulfonate:



2) Preparation of basic calcium sulfonate:



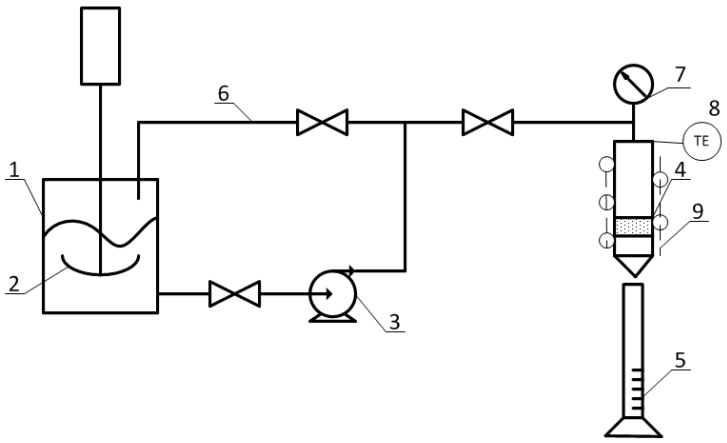
3) Preparation of calcium acetate:

$$2CH_3COOH + Ca(OH)_2 = (CH_3COO)_2Ca + 2H_2O \quad (3)$$

As part of the study, a number of SLCS (with the active substance content of 42% wt.) syntheses were carried out using variable amounts of acetic acid relative to the amount of calcium hydroxide used in the synthesis (see reactions 1,2).

After completion of the synthesis process, 100 ml of the product was centrifuged to determine the volume fraction of sediment. Also, after completion of the synthesis process, the SLCS solution was subjected to the removal of toluene and water on a vacuum rotary evaporator at 150°C and 15 kPa since, according to literature, even a small amount of water can significantly impair the filterability of the product [2].

The dehydrated product was then filtered in an apparatus simulating the operation of a press filter (Figure 1). Filtration was carried out at elevated temperature (in the range of 80 – 90°C) and at 0,2 MPa. A diatomaceous earth fill layer was used as an aid. The layer was poured over ashless paper filter.



1 - tank; 2 - mixing device; 3 - pump; 4 - pressure vessel with support for the filter; 5 - measuring cylinder; 6 - filtrate circulation line; 7-manometer; 8 - electric heater; 9 - thermocouple with temperature indication

Figure 1. – Sketch of a laboratory filtration unit

Results and discussion. The preferred kinematic viscosity of the low alkaline sulfonate additives at 100°C is 300 cSt or less, most preferably 30-100 cSt. The volume fraction of sediment in the product before filtration in the most preferred variant is in the range from 0,1 to 0,6% vol. To establish the filtration intensity, the volume filtration rates were determined and the filtration diagrams for three samples were plotted (Fig. 2). On that basis, to compare the obtained filtration results, such terms as "well-filtered sample" and "poorly filtered sample" were introduced.

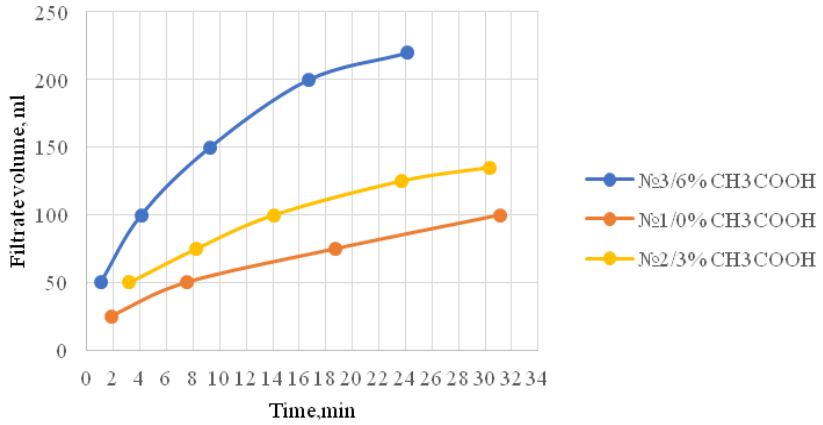


Figure 2. – Filtration diagrams of SLCS samples

The attempt to filter sample №1 was unsuccessful due to the high sediment content in combination with high viscosity, the observed filterability was unsatisfactory. This example shows that the preparation of low alkaline calcium sulfonate from high molecular weight sulfonic acid in accordance with the known [2] method, using the raw materials adopted in this study, leads to the formation of an unfilterable product. The observed filterability in the case of samples №2 and №3 improved as evidenced by the positive dynamics of the volume filtration rate increase compared to sample №1. However, during the filtration of the sample № 2 the filter quickly clogged as can be seen from the fall-off in the volume filtration rate. Physicochemical quality characteristics of the filtered samples are presented in the Table 1.

Table1. – Quality characteristics of SLCS samples

Characteristic	Sample number		
	№ 1	№ 2	№ 3
Observed filterability	Poor	Poor	Good
Volume fraction of sediment, % vol.	3,50	1,50	1,00
Volume filtration rate, ml/hour	192,93	266,89	547,72
Total base number, mg KOH/g	3,72	7,48	12,58
Total acid number, mg KOH/g	1,87	2,07	2,00
Kinematic viscosity at 100 °C, cSt	760,00	561,00	356,00

There are trends of decrease in the volume fraction of sediment and the kinematic viscosity of the obtained products with the increase of the acetic acid amount. The increase in alkaline number is due to an increase in the amount of calcium acetate in the product.

For the filtered samples the average size of the dispersed particles was determined using DLS spectrometry. The results are presented in figure 3.

As can be seen from the PSDs of the obtained samples, the amount of small-sized dispersed particles tends to decrease as the acetic acid content in the starting mixture increases.

Analyzing the total results one can conclude that in the synthesis of SLCS based on high molecular weight dialkylbenzenesulfonic acid, the addition of some carboxylic acid, in particular acetic acid, has a positive effect on the quality of the product. The tendency to form gel-like viscous products is reduced. The product has better filterability than the product obtained according to the existing technology. However, not all quality characteris-

tics have reached acceptable levels. The product still has too high viscosity and a volume fraction of sediment. This article does not establish the exact reasons for all the above-mentioned facts - this will be the basis for further research.

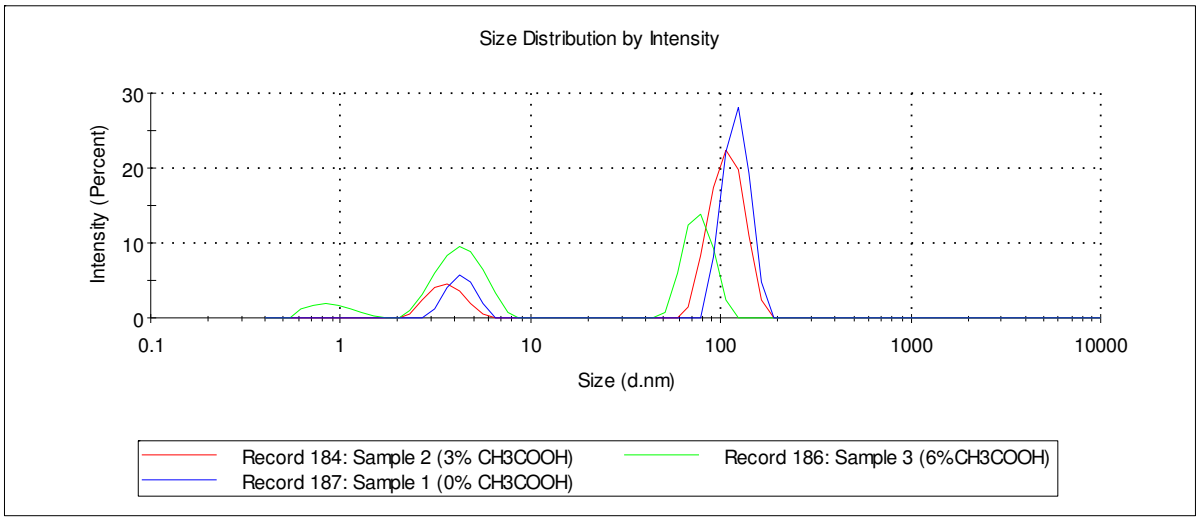


Figure 3. – Particle size distributions (PSDs) for the obtained SLCS samples

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