

Getting Viscous Additives from Heavy Oil Fraction

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Abstract: To improve the viscosity and improve the rheological characteristics of the produced oil in fields with heavy, high-viscosity oil, a number of technologies are used. Heat treatment and other methods of physical exposure; dilution with light fractions of oil or various solvents, as well as the introduction of additives that regulate the viscoelastic properties of the oil. The work considers nonionic and anionic surfactants that are obtained from petroleum products. Alkyl aromatic and alkyl naphthenic-aromatic hydrocarbons in the heavy oil fraction are the most important that produce fat-soluble additives.

Keywords: oil, surfactants, viscosity, sulphonyls, alkyl sulfonate, colloidal system, sulfonation

1. Introduction

High paraffin content in oil complicates and increases the cost of its production, transportation and processing. During the extraction and pumping of high-paraffin oil, paraffin is deposited on the pipe walls. In main pipelines, the thickness of paraffin deposits reaches 30 mm [1]. A feature of the rheological properties of these oils is manifested in the inconstancy of their dynamic viscosity, which depends on the applied shear stress and fluid velocity. Such a flow of oil is non-Newtonian and is determined by its colloidal-chemical state (composition of the dispersed phase and dispersion medium), the nature of intermolecular interactions, and structure formation [2].

According to the literature, there are various classifications of oils by paraffin content. In [3], it is proposed to divide oils according to the paraffin content into three classes: low-paraffin (paraffin content less than 1.5%), medium-paraffin (1.5% to 6%) and paraffin (more than 6%). Here, the threshold values are determined taking into account the industry standard IS-38.01197-80. In accordance with State Standard Russia 51858-2002, we will further consider oil as paraffin if the paraffin content in them is more than 6%.

Currently, a very large number of surface-active substances (SAS) are used in the oil industry, but high molecular weight polymeric compounds of various types are most widely used [4]. In particular, copolymers of alkenes with vinyl acetate, with unsaturated acid esters (e.g. acrylic or meth-acrylic), etc. are widely used.

Alkylating alkylaromatic and aromatic hydrocarbons in heavy petroleum fractions are the most important that produce fat-soluble surfactant. Currently, important that the use of sulfo-derivatives of these heavy fraction as an additive. Sulfonation is a difficult process. In practice, alkyl aromatic hydrocarbons are sulfonated with various sulfo agents: concentrated sulfuric acid, oleum (solution of sulfuric anhydride in sulfuric acid monohydrate), vapor 100% sulphuric anhydride [5].

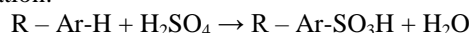
Oleum reacts vigorously with olefinic hydrocarbons, so the reaction is carried out at low temperatures. When using oleum and sulfuric anhydride side reactions occur, such as

oxidation and tarring. Due to the high activity of these reactants in the sulfonation are formed a number of sulphaneole, polysulfones of the isomeric sulfonic acids, these reactions to olefinic hydrocarbons is observed to a small extent [6].

2. Materials and methods

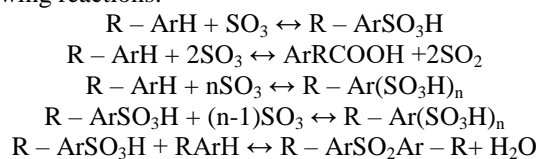
Taken in response to the amount of 95% sulfuric acid was varied from 1.2 to 1.8 in the molecular ratio of alkylaromatic. While the rest of the reaction conditions of sulfonation was left constant: temperature 55-65°C, the duration of the sulfonation 120 min.

The introduction of sulpho groups in the aromatic nucleus with sulphuric acid can be represented in General form by the equation:



where; R is an alkyl radical containing 9 to 15 carbon atoms;

Ar – is an aromatic nucleus consisting of a benzene derivative, naphthalene, anthracene. Also, you can occur the following reactions:



According to the influence of the quantity of sulfuric acid to sulfonation reaction, the optimal molar ratio of alkylaromatic hydrocarbons of the extract and 95% sulfuric acid is 1:1,54-1,8. With the increase in the number sulfureuse agent, exit alkylaryl facility increased from 74,6 to 90.8 mass. % basedonalkylaromatic.

Table 1: Indicators of sulfonation of alkyl aromatic hydrocarbons extract oil

Material balance and exit	The molar ratio of alkyl aromatics to sulfuric acid		
	1:1,2	1:1,5	1:1,8
Taken, g:			
Extract 60% alkylaromatic hydrocarbons	750	750	750
95% sulfuric acid	177,6	220,8	265
Water for separating waste acid	600	600	600

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Received, g:			
Alkylarylsulfonicacid	522	579	632
Wastesulfuricacid	505	526	549
Non-sulfonatednaphthenicparaffins	483	447	416
Losses	17,6	18,8	18
The composition of alkylarylsulfonic acid, %:			
Activesubstances	78,0	78,4	78,1
Unreactedhydrocarbons	1,8	1,2	1,1
SulfuricAcidResidues	0,2	0,4	0,8
Ash	20	20	20
The output of alkylarylsulfonic acid., Wt.% alkylaromatics	74,6	81,6	90,8

Reactivity of sulfuric acid can vary with the dilution of its reaction with water and studying the process of sulfonation is heterogeneous, the study of the kinetics of the sulfonation was carried out at constant volume of the extract and with a large excess of sulfuric acid. It should be noted that the sulfonation of alkyl aromatic hydrocarbons of the extract at low temperatures requires a longer time, a rise in temperature above 65°C leads to an acceleration side sulfonation process (as oxidation, condensation and polymerization, and the formed acid sludge).

Department of alkylarylsulphonate from naphthenoaromatic hydrocarbons and spent sulfuric acid. The separation of sulphonic acids from sulfones containing a large amount of spent sulfuric acid is a much difficult process. The simplest allocation method of the sulfonic acid is a dilution of sulfatase water [7]. Also can be neutralized with tertiary amines, such as trimethylamine, a triethylamine, triethanolamine or pyridine. After neutralization the mass was kept in separating funnel. Stratification occurs within 30-60 min and the mass is divided into two layers: 1) the bottom layer is the neutralized product, mainly salts alkylarylsulfonate; 2) the top layer of unreacted hydrocarbons. The product is a dark brown pasty mass, readily soluble in the heavy oil fraction, the water and polar organic solvents, insoluble in diethyl ether.

Study of the influence derived surfactant on the viscosity high paraffin oil. To study the influence on the viscosity of the resulting refined products such as waxy oil. Physical indicators of high-wax oil and the model oil are shown in the following table:

Table 2: Physical indicators of high-wax oil and model oil

Indicators	High paraffin oil	Oil product (sample-1)	Oilproduct (sample-2)
Viscosity, MPa * s	1090	815	984
Density, g / cm ³	820	832	814
Color	Darkbrown	Darkbrown	Darkbrown
Paraffins, wt.%	6,96	7,64	7,25
Asphaltenes, wt.%	0,73	0,78	0,68
Resins, wt.%	4,34	5,64	4,78

The viscosity of petroleum products was checked by adding from 1% to 5% of the synthesized surfactant to the oil. According to the results, a surfactant that is obtained from a heavy oil fraction significantly reduces viscosity.

Table 3: Change in viscosity when alkylarylsulfonic acid is added to highly paraffinic oils

Added surfactant	Viscosity, MPa * s		
	Oil product (sample-1)	Oil product (sample-2)	High paraff. Oil (according to literature)
preliminary viscosity	815	984	1090
1 %	354	362	348
2 %	285	294	306
3 %	268	277	274
4 %	265	275	272
5 %	264	274	271

Based on laboratory tests, the obtained samples of alkyl- and alkyl-aryl sulfonic acids lowered the viscosity of high-viscosity oil products, which are shown in table-3.

3. Conclusion

From the results it can be concluded that adding a synthesized additive to the initial solution up to 3% is enough. The paraffinic oils themselves can be used as raw materials, obtaining new types of surfactants and low cost, allow you to effectively master its production. And also use it in the transportation and production of high viscosity oils.

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