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Influence of the additives of natural sulphur-organic compounds on thermal stability of oil fractions of arlan petroleum

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Abstract. The influence of additives of natural sulfur-organic compounds on the thermal stability of the oil fraction of Arlan petroleum in an electric field is studied.
It has been established that the introduction of additives of natural sulfur-organic compounds into the petroleum fraction leads to a decrease in the formed solid sediment and acid number, which indicates an increase in the dielectric characteristics of the oil and an increase in its thermal stability in the electric field.
The optimum amount of addition of natural sulfur-organic compounds in an amount of 0.5% reduces the amount of water-soluble acids formed, and, consequently, also the aging of the oil.

Introduction

Transformer oil of petroleum, widely used in power engineering as a heat sink and insulating medium, under the influence of high temperatures, electric field and molecular oxygen of air is subject to aging [1]. As a result of the aging of the oil its performance properties deteriorate [2, 3]. To improve the performance of the transformer oil, various types of additives are used.

The increase in the extraction and processing of sulfur and high-sulfur petroleum, set the task of using sulfur-organic compounds in industry and agriculture. Organo-compounds having unique properties can be widely used as various types of additives for transformer oils to improve their performance properties.

Experimental part

The purpose of this work is to study the effect of natural sulfur-organic compounds on the performance properties of transformer oil.

The object of the study was the oil fraction with Tkip = 300-400 ° C Arlan oil. Natural organosulfur compounds were obtained by adsorption separation of the oil fraction on silica gel ASK and aluminum oxide.

In the process of adsorption separation of the oil fraction on the adsorbents used, five fractions of organosulfur compounds were isolated. Physicochemical characteristics of organosulfur compounds isolated from the oil fraction of Arlan oil are given in Table 1.

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Table 1

Physico-chemical characteristics of sulphur-organic compounds oil fraction of Arlan petroleum

Indicator name	Fraction of sulphur-organic compounds				
	I	II	III	IV	V
Density ρ_4^{20}	1,0	1,0320	1,0310	1,1070	1,0827
Refractive index	1,5560	1,5740	1,5830	1,680	1,6270
Molecular mass	321	302	260	227	213
Sulphur content, %					
common	11,3	8,1	7,4	10,1	7,9
sulphide	10,9	7,6	6,2	отс.	отс.
Percentage of sulfide sulphur from total	96,5	93,8	83,8	-	-
The empirical formula	$C_nH_{2n-5}S$ n=21	$C_nH_{2n-8}S$ n=20	$C_nH_{2n-10}S$ n=17	$C_nH_{2n-15}S$ n=15	$C_nH_{2n-15}S$ n=14

From the experimental data given in Table 1 it follows that fractions I-III with a total sulphur content of 11.3% to 7.4% consist of 96.5% -83.8% of sulfides.

According to IR spectroscopy, the presence of an absorption band in the region of 1170 cm-1 indicates the presence of alkyl substituted mono-cycloalkanes. The absorption bands in the region of 775 cm^{-1} and 745 cm^{-1} indicate the presence of sulfides, respectively, with propyl and butyl radicals. The characteristic absorption bands for aromatic hydrocarbons were not detected by IR spectroscopy.

As a result of the investigation of fractions I-III by mass spectroscopy, it was found that the sulfides in these fractions are represented by saturated compounds, mainly thiamono- and thiabicycloalkanes in the absence of uncondensed bi- and tricyclic sulfides.

From Table 1 it follows that the organosulfur compounds of fractions IV and V do not contain sulfide sulfur in their composition. Fractions IV and V by the ratio of carbon to hydrogen can be represented by the empirical formula $C_{15}H_{15}$, which corresponds to thiophene derivatives with condensed benzene nucleus.

Using IR spectroscopy in IV and V fractions, absorption bands were observed in regions 2955, 2921 and 2873 cm^{-1}, as well as in the 1587, 1481 and 1280 cm^{-1} regions, indicating the presence of thiophenes and their derivatives.

In the UV spectra, an intense band of 240 nm is detected, which indicates the presence of polyalkyl-substituted thiophenes. PMR spectra in the range of 0.9 and 1.21 ppm. correspond to the protons of the saturated thiophene ring and its alkyl substituents, and the signals are 1.92 and 2.18 ppm. indicate the presence of methyl substituents thiophene ring.

Fractions IV and V are probably polyalkyl substituted thiophenes and cyclothiophenes with various substituents.

Mass spectroscopic analysis of organosulfur compounds of fractions I-V showed that in these fractions there are compounds corresponding to the empirical formulas shown in Table 1.

The bulk of fraction I is represented by saturated organosulfur compounds - sulfides, the empirical formula of which C_nH_{2n-5} S indicates their cyclic structure.

In the fraction II, the compounds of $C_nH_{2n-8}S$ are represented by thiaindans. The remaining compounds represented by the general formulas $C_nH_{2n-10}S$ and $C_nH_{2n-15}S$ refer to alkyl-, cyclo- and bicyclobenzobenzothiophenes.

The fractions of organosulfur compounds I-V were used as an additive to the desulfurized oil fraction (sulfur content was 0.001%) to study the change in its performance properties.

Investigation of the operational properties of the desulfurized oil fraction in the presence and absence of additives of fractions I-V was studied in an apparatus described in the literature [4]. The amount of additives introduced into the desulfurized fraction varied within a wide range from 0.1% to 1.1% in 0.2% increments. The effect of the number of additives of fractions I-V was investigated by the amount of precipitate formed and the acid value, which were determined according to GOST 6370-83 and GOST 6307-75, respectively.

The obtained experimental data on the effect of additives of fractions I-V on the thermal stability of the desulfurized oil fraction determined in accordance with GOST 982-80 are shown in Fig. 1,2.

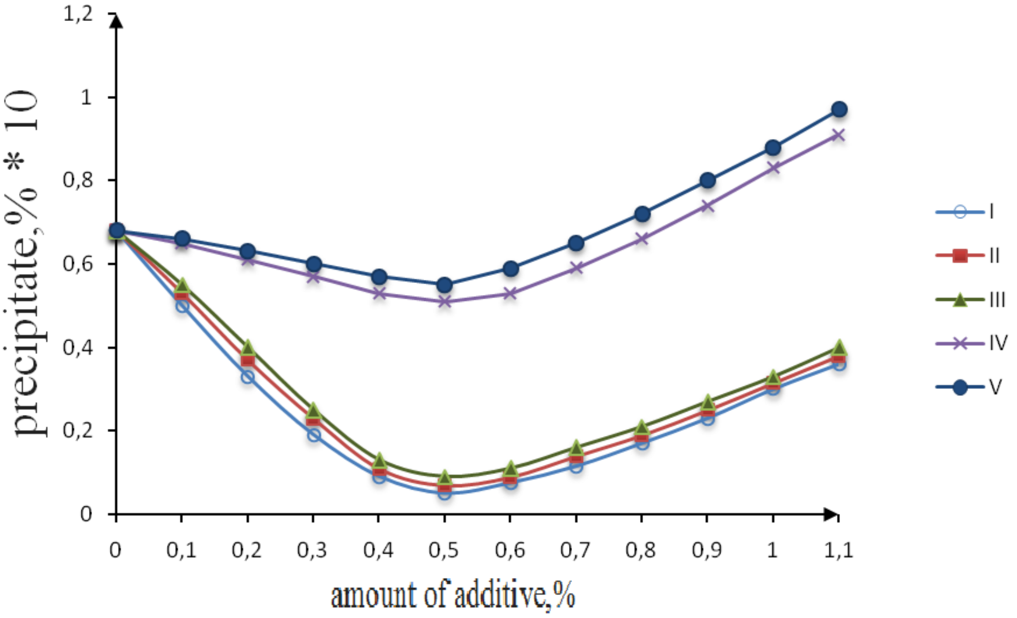

Fig.1. The effect of additives I-V on the amount of precipitate formed with aging of oil fraction

From the experimental data shown in Fig. 1, it can be seen that the additives I-III, consisting mainly of sulphides, refer to effective antioxidant additives, since in the presence of the latter from 0.1% to 0.5% the amount of precipitate formed decreases for all additives (I-III). The amount of solid precipitate formed in fractions I, II and III at an additive concentration of 0.5% was 0.005%, 0.007% and 0.009%, respectively. A further increase in the number of additives (I-III) to 1.1% contributes to the increase in the precipitate formed to 0.037%, 0.038% and 0.039%, respectively.

It also follows from figure 1 that the fractions of organosulfur compounds IV and V, which do not contain sulfide sulfur represented by benzothiophene derivatives, increase the thermal stability of the oil fraction by 1.58 times and 1.4 times, respectively. However, the greatest antioxidant effect at which a minimum amount of precipitate is formed, 0.058% and 0.06%, is achieved with the content of 0.5% additive IV and V in the oil fraction. Increase in the amount of additive of fractions IV and V from 0.5% to 1, 1% contributes to an increase in the amount of sediment to 0.13%, 0.15%. Consequently, the optimum amount of additive of organosulfur compounds of fractions IV and V is 0,5%.

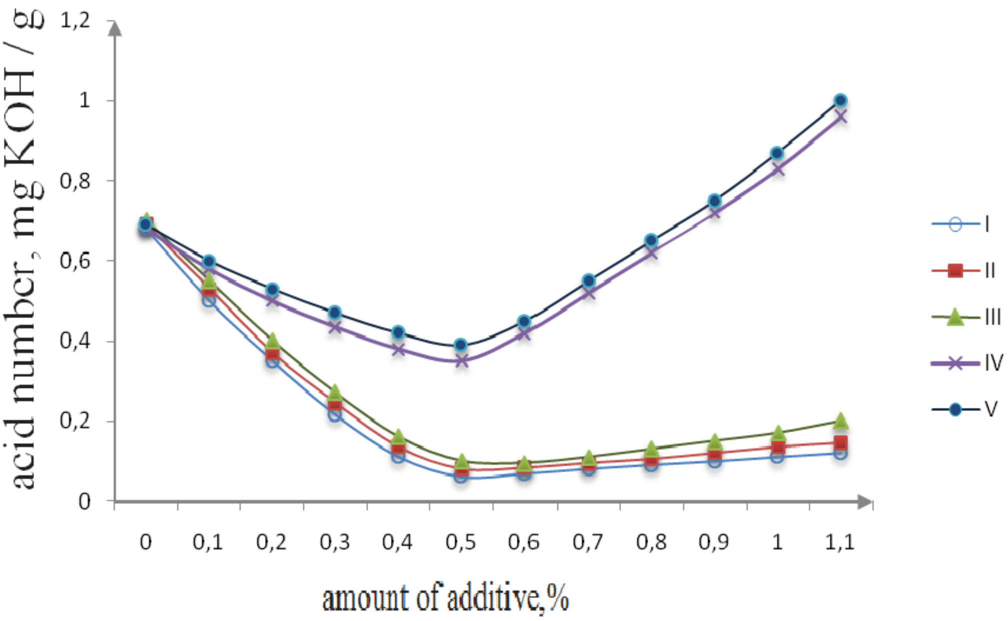

Fig. 2. The effect of the number of additives I-V on the acid number

It can be seen from the data in Fig. 2 that with an increase in the concentration of additives I-III from 0 to 0.5%, the acid number decreases from 0.068% to 0.006%, 0.008% and 0.01%, respectively, for all the investigated additives I-III. The increase in the concentration of additives I-III in the oil fraction from 0.5% to 1.1% is accompanied by an increase in the acid number, respectively, to 0.0105, 0.0146 and 0.02 mg of KOH / g fraction. This fact points to the inexpediency of increasing the concentration of additives I-III in the oil fraction.

The fractions of additives IV and V under identical experimental conditions in accordance with GOST 982-80 show inertness in the process of increasing the thermal stability of the oil fraction in comparison with the additives I-III. The acid number in the presence of additives IV and V in an amount of 0.5% decreases, respectively, to 0.034 and 0.038 mg KOH / g fraction. The course of curves I-III and IV-V is identical, which indicates the same nature of the effect of additives on the oxidation of oil hydrocarbons. The optimal amount of IV-V additives is also 0.5%.

Under the influence of an electric field, increased operating temperatures and structural materials such as metals, cellulose and varnishes, the transformer oil is aging. As a result of the aging of the oil, a precipitate forms and the acid number increases. Precipitation precipitates the aging of cellulose solid insulation and reduces the heat transfer rate, which worsens the insulating properties of the oil. The acid number refers to the important characteristics of the oil, since it indicates the presence of oxidation products of the hydrocarbons that make up the oil, and therefore its oxidation stability.

From the studies carried out it follows that the best antioxidant additives to the oil fraction are fractions I-III, consisting of oil sulphides. The additive fractions IV and V, which are derivatives of thiophene with condensed benzene nucleus, exhibit less antioxidant properties with respect to the oxidation of hydrocarbons in the oil fractions.

The formation of low molecular weight volatile acids during the aging of transformer oil leads to an increase in the oxidative conversion of its hydrocarbons, aging of solid insulation and corrosion of the metal. In this connection, the influence of additives of fractions I-III on the formation of volatile acids was studied. The study was carried out in accordance with GOST 982-80 in the presence of 0.5% of the additives of fractions I, II and III, respectively, to the desulfurized initial fraction of Arlan petroleum.

The results of the study are shown in Table 2.

Table 2

Effect of additives of sulphur-organic compounds on the formation of water-soluble acids

Oil fraction	Stability in accordance with GOST 982-80 for the content of water-soluble acids	
	Nonvolatile	volatile
Original oil fraction	0,0045	0,0059
Oil fraction + 0,5 % fraction I	0,0030	0,0019
Oil fraction + 0,5 % fraction II	0,0035	0,0022
Oil fraction + 0,5 % fraction III	0,0037	0,0026
Requirements according to GOST 982-80	0,005	0,005

From the data in Table 2 it follows that all the additives of fraction I-III contribute to reducing the amount of water-soluble acids formed.

Conclusions

1. The influence of natural sulphur-organic compounds on the increase of thermal stability of the oil fraction of Arlan petroleum was studied.
2. An optimum number of additives to be studied is found to be 0.5%, at which the thermal stability of the oil fraction increases.
3. It has been established that the investigated additives of fractions I-III, taken in an amount of 0.5%, reduce the amount of water-soluble acids formed, which increases the thermal stability of the oil fraction.
4. It has been established that the fractions of natural sulphur-organic compounds containing sulfide sulfur are the most effective additives to the oil fraction.

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