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PROPERTIES AND THERMO-OXIDATIVE STABILITY OF THE DEWAXED RESIDUAL PRODUCT OF THE VACUUM GAS OIL HYDROCRACKING PROCESS

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The actual problem of oil oxidizability after hydrogenation and cleaning processes is considered. The separation capacity of various adsorbents is analyzed. The group composition of oils and its effect on stability are analyzed. The main theories of oxidizability, mechanisms and causes are also considered. The thermal stability of the dewaxed residual product of vacuum gas oil hydrocracking after purification and with the introduction of an inhibitor was analyzed.

Introduction. The use of hydrogenation processes in the production of base oils makes it possible to obtain high-quality hydrocracking commercial oils with improved technical characteristics compared to traditional mineral oils. Hydrocracking base oils have a high viscosity index, better injectivity to additives, and are more environmentally friendly [1,2].

However, deep cleaning has a very important drawback: oils are characterized by low resistance to auto-oxidation by air oxygen during storage, which leads to a change in their color and chemical composition, increased corrosion activity, and sediment formation [3].

During hydrocracking, raw materials undergo a complex of complex chemical transformations that lead to a significant change in their group composition, including the redistribution of various groups of hydrocarbons into fractions. In this regard, we can expect that the fraction isolated from the hydrocracking residue by vacuum distillation, will vary not only by boiling temperatures, but the content of different groups of hydrocarbons, and therefore, have different physical and chemical properties, which further affect the properties of the produced oils and their operating characteristics [4].

This article discusses the main properties of the dewaxed residual product of the hydrocracking process of vacuum gasoils, the group composition, the distribution patterns of hydrocarbons and their thermal and oxidative stability, and the effect of inhibitors on oxidizability.

Research part. It is known that the stability of different groups of hydrocarbons differs from each other. The main components of petroleum oils are hydrocarbons that simultaneously contain naphthene-paraffin, paraffin-aromatic, or paraffin-nafteno-aromatic structural elements. In addition to hydrocarbons, oils also contain a variety of heteroorganic compounds containing sulfur, oxygen, nitrogen, and various metals. All this makes it very difficult to study the dependence of the operating properties of oils, including stability against oxidation.

According to one of the first studies, it can be said that aromatic hydrocarbons that do not have side chains have the greatest stability to oxidation. As the number of cycles increases, the stability against oxidation decreases. Hydrocarbons containing both aromatic and naphthenic cycles are less stable than aromatic ones.

Naphthenic-aromatic hydrocarbons are actively oxidized with the formation of a number of products, including resins. Naphthenic and paraffinic hydrocarbons of oils are less stable than aromatic ones during a significant oxidation time and form mainly acids and hydroxyacids.

The stability of the mixture of saturated and aromatic hydrocarbons is not additive. It is mainly determined by the amount and especially the structure of the aromatic hydrocarbons contained in them. When 1-10% aromatic hydrocarbons without side chains or with short side chains, as well as hydrocarbons containing phenyl radicals, are introduced into the fraction of saturated hydrocarbons, the oxidation of the mixture is sharply inhibited. Fractions of aromatic hydrocarbons with long side chains are effective only at a concentration of more than 20% by weight. [4].

Thus, aromatic and naphthenic-aromatic hydrocarbons in optimal concentrations are natural oxidation inhibitors. The reason for this action is the formation of phenols, quinolines, quinones and resinous products, which also act as inhibitors.

In this work, the initial dewaxed hydrocracking residue was purified using various adsorbents: granular active clay and ASCG grade silica gel.

The nature and size of the adsorbent pore surface are crucial factors determining the adsorption efficiency. The size of the adsorbed molecules is also important. Coarse-pored and fine-pored adsorbents, all other things being equal, equally adsorb surfactants consisting of small molecules, and in different ways – substances whose molecules have large sizes. If the size of the molecules of the adsorbed substances exceeds the pore size of the adsorbent, the efficiency of the adsorption process decreases. As a rule, coarse-pored adsorbents are used for oil adsorption purification [5].

It was found that granulated active clay has a greater separating ability in relation to the components of the group composition of the hydrocracking oil under study than silica gel of the ASKG brands. This is due to the increased pore size of the active clay and higher acidity, due to which the active clay exhibits an increased polarizing ability.

The main changes in the characteristics after cleaning the initial dewaxed hydrocracking residue with active clay in an inert medium are shown in Table.

Table. – Sample properties

Indicator	Value for the sample		Changing
	before cleaning	after cleaning	
Refractive $index\ N_D^{20}$	1,4652	1,4644	-0,0008
Color according to ASTMD1500 (STB 1796)	1,5	less than 0,5	–
– Density at 20°C, kg / m^3	843,3	841,6	-1,7
– Density at 15°C, kg / m^3	846,6	844,9	-1,7
– Solidification temperature, °C	minus 15	minus 15	0
– Iodine number, gJ2 / 100 g	0,70	0,20	-0,5
– Acid number mg KOH/g	0,65	0,31	0,34
Kinematic viscosity at:			
– 40 °C,^{mm2}/ s	23,52	23,44	-0,08
– 100 °C,^{mm2}/s	4,71	4,70	-0,01
Viscosity index	120	120	0
Group composition (wt%):			
– naphthenic-paraffinic hydrocarbons	98,3	99,74	1,44
– aromatic hydrocarbons	0,75	0,17	-0,58
– resins	0,95	0,09	-0,86

The hydrocracking residue is characterized by a low total content of aromatic hydrocarbons. The residual product of the hydrocracking process contains mainly aromatic compounds of group I with an interval of refractive index change at 20 °C from 1,49 to 1,53 [6]. In the remainder of the Unicraking process, aromatic hydrocarbons are mainly represented by more stable monocyclic compounds, i.e. benzene derivatives. This pattern can be traced by analyzing the spectra.

Also, it is impossible not to take into account the effect of sulfur compounds on the oxidizability of oils. The oils contain approximately equal amounts of sulfides and residual sulfur compounds. Organic sulfides are more easily oxidized than hydrocarbons, and with a low content in oils, it slows down oxidation.

In addition to the above components, the oxidation of oils is affected by resinous-asphaltene substances. Petroleum resins in concentrations of up to 1% stabilize the oil, with a further increase in the concentration, their effectiveness decreases, and sometimes the oil's oxidizability increases. This phenomenon may be related to the formation of asphaltenes [7].

To study the thermal and oxidative stability of oils, it is necessary to consider the oxidation mechanism directly in more detail. Modern ideas about the mechanism of hydrocarbon oxidation processes are based on the peroxide theory of autooxidation by A. N. Bach and K. Engler and the theory of chain reactions developed by N. N. Semenov and his school.

According to the peroxide theory, the first oxidation products are peroxides and hydroperoxides. According to these propositions, oxygen activation occurs as a result of breaking one bond between atoms in an oxygen molecule, which requires less energy than complete dissociation of the oxygen molecule. The active oxygen molecule easily combines with combustible substances without breaking down into atoms.

The energy of breaking the —O—O bond in peroxides and hydroperoxides is much lower than in the oxygen molecule, so they are very reactive and poorly stable. When heated and exposed to mechanical forces, they easily disintegrate to form new substances or radicals. The radicals formed during the decomposition of peroxides are the active centers of oxidation reactions [8].

In paraffinic and naphthenic hydrocarbons, the tertiary CH group is most easily oxidized. The quaternary carbon group does not oxidize itself and prevents the oxidation of those closest to it C-H groups (even tertiary ones).

However, the peroxide theory of oxidation is not able to explain the existence of the induction period. This was explained by the doctrine of chain reactions.

According to N. N. Semenov, a branched chain process generates active particles in a substance - free radicals, the number of which increases rapidly in time due to branching of the chain.

This oxidation process can be divided into three periods: the first is the induction period. During this period, no visible changes are observed, and compounds that change the characteristics of oils do not accumulate. After the end of the induction period, active interaction with oxygen begins, oxidation is initiated, and the formation of primary oxidation products – hydroperoxides-occurs. Decomposition and oxidation of hydroperoxides leads to the appearance of acidic and neutral oxidation products.

The next stage is the formation of precipitation. Depending on the base of the oil, different products can be formed and in different proportions [7].

The accumulation of R-O-O-H hydroperoxide in the system, which is the main intermediate product of oxidation, causes auto-acceleration of the process, since it decomposes with the formation of free radicals. After the formation of hydroperoxides, products of deep oxidation appear. Numerous experimental data indicate that alcohols, ketones, aldehydes, and carboxylic acids are the final decomposition products of hydroperoxides. In addition, peroxides can enter into condensation reactions with carbonyl compounds to form oxy-alkyl peroxides that break down into acid, aldehyde and hydrogen.

Among other factors that accelerate the process of oil oxidation, the role of the oil contact surface with air or oxygen should be noted. The larger this surface area, the correspondingly more intense the oxidation. The oxidation rate also depends on the rate of oxygen diffusion into the oil. Also surface metals have obvious catalytic actions. Most actively accelerate the oxidation process of chalk, lead and their alloys, manganese, chromium; a little less – iron and tin. Organic salts of copper, iron, manganese, silver, and cobalt cause heavy precipitation during oil oxidation.

The easiest way to increase the oxidation resistance of oils is to add anti-oxidation additives. Let's consider their effectiveness in comparison with samples without an inhibitor.

The research was conducted in accordance with GOST 20354-74. Methods for determining evaporation in cups.

Object of research: dewaxed residual product of the hydrocracking process after adsorption purification.

As can be seen from the results obtained (Fig. 1), the lowest deviation from the initial sample is the depreciation curve with a temperature control time of 30 minutes. A further increase in time leads to intensive oxidation and, as a consequence, a decrease in transmission coefficients. Compared to the original oil sample, the transmittance at lengths of 400 and 450 nm from 59,4/98,2 approached very low values of 0/0,4. The change in these indicators for a sample that was thermostated for 30 minutes is more abrupt than for samples of 60 and 240 minutes. This may be due to the accumulation of oxidation products in the medium, which act as natural inhibitors.

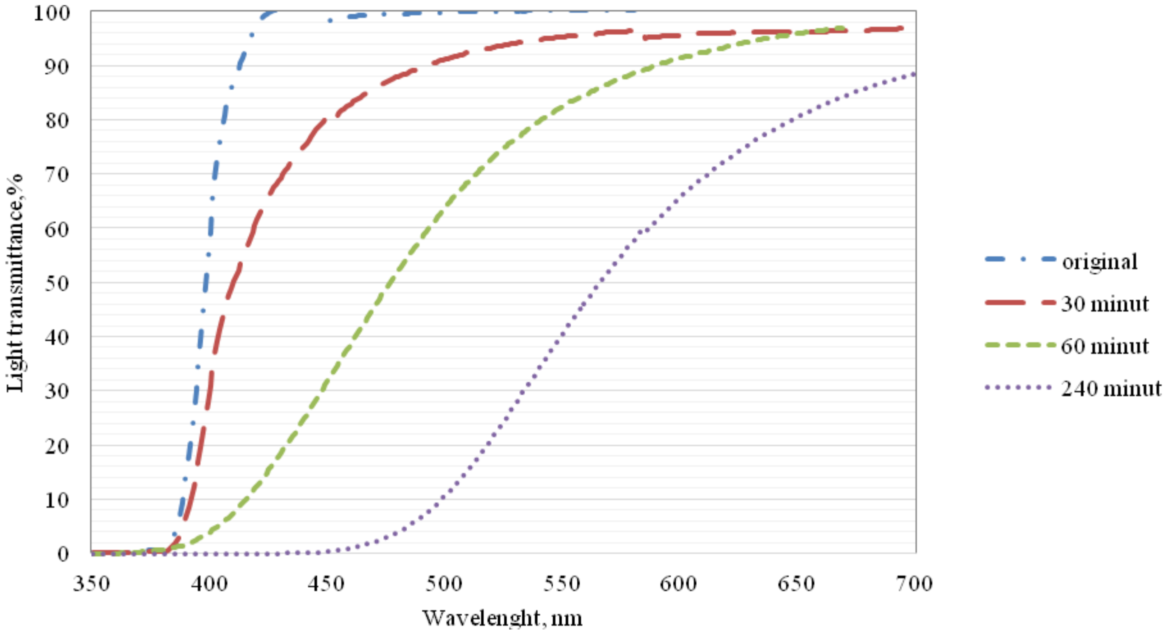

Figure 1. - Dependence of the transmission coefficient on the wavelength and temperature control time of samples

Next, we consider the effect of the duration of heat treatment on the properties of the purified dewaxed residual product of the hydrocracking process of vacuum gas oils in the presence of 0,5% by weight.an inhibitor (Fig.2).

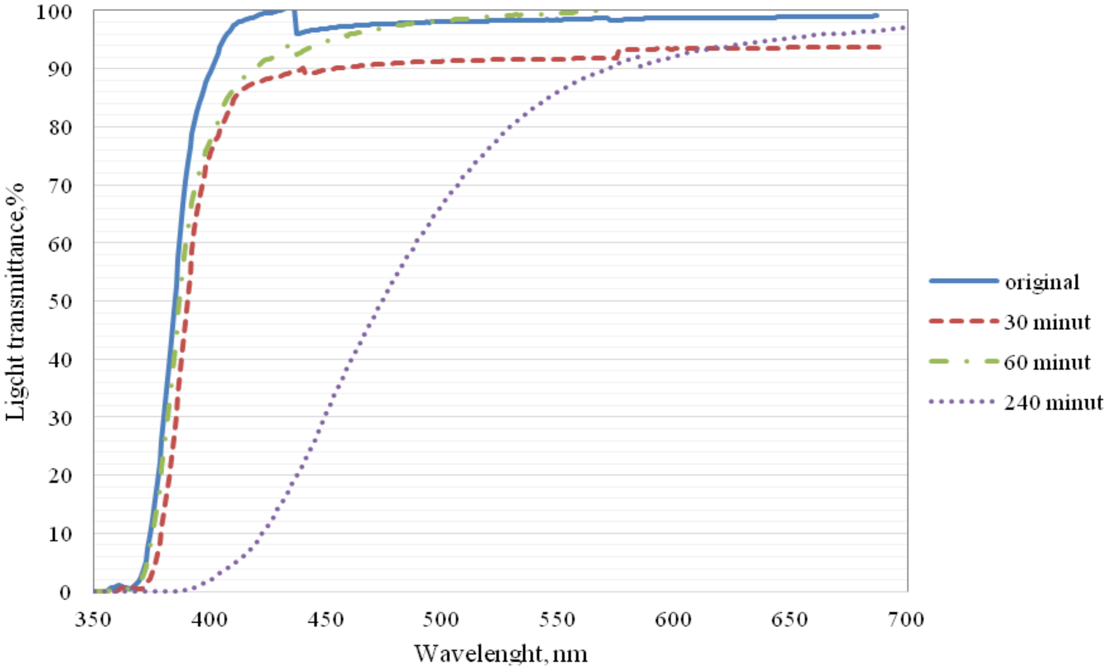

Figure 2. - Dependence of the transmission coefficient on the wavelength and temperature control time of samples

After analyzing the results, we see that the curves of the oil samples, which are thermostated for 30 and 60 minutes, have small deviations from the original sample. If we compare the results of the samples with the inhibitor and without-noticeable improvements in the thermal-oxidative stability in terms of light transmittance and color indicators.

Conclusion. Based on the analysis of the results of the group composition from the hydrocracking residue, it can be concluded that the total content of aromatic hydrocarbons is low. The residual product of the hydrocracking process contains mainly aromatic compounds of group I, represented mainly by benzene derivatives. According to the peroxide theory and the chain reaction theory, oxidation develops due to the formation of peroxide compounds and free reactive radicals. The oxidation process is provoked by such factors as: increased temperature, light radiation, catalyzing metals in the composition of the contacting surfaces. The conditional process It can be divided into three stages: induction period, initiation period and stabilization period. The main task is to increase the first period, increase stability during operation in conditions of suspended rigidity. This can be done by adding oxidation inhibitors. According to the results of studies, the introduction of an anti-oxidative additive improves the stability of samples in comparison with oils without it.

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