Production of binding materials based on high-viscosity oils and natural bitumens

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Abstract. Due to the growing market demand for road bitumen, there is a need to increase the rate of its production. Among the promising technologies currently available, the oxidation of heavy hydrocarbon raw materials with air oxygen is the most optimal technology for producing bituminous binders. In turn, substandard oil reserves are suitable raw materials for this process. Thus, the study of the regularities between the composition of the oxidation products of ultra-viscous oil and the physicochemical properties of the oxidation conditions will contribute to the development of the binding materials production technology.

1. Introduction

Thorough and environmentally friendly processing of ultra-viscous oils and natural bitumens is achieved in conjunction with the development of solvent and hydrogenation technologies aimed at expanding the raw material base for thermocatalytic secondary oil refining processes, the development of technologies for obtaining bitumen binders based on heavy residues from the primary processing of ultra-viscous oils and natural bitumens [1]. Unlike conventional oils, which are low-and medium-concentrated colloidal systems - sols, ultra-viscous oils and natural bitumens are highly concentrated dispersed systems - gels, which are suitable raw materials for obtaining bituminous binders.

Bituminous binders are one of the multi-tonnage petroleum products, and, at the same time, they are scarce [2,3]. The share of production of bitumen binders for road use from the total amount of processed conditioned oil in the country is not more than 3%, while the total demand for road bitumen is met by 60%. While there is a growing turnover of road transport, a significant increase in the Russian car fleet requires the reconstruction of existing roads and the construction of new ones. The growing consumption of road bitumen requires an increase in their production volume. Currently several technologies have been developed to produce road bitumen: production of residual (non-oxidized) road bitumen by deep atmospheric-vacuum distillation or extraction (solvent technologies), compounding of high-boiling residues of atmospheric-vacuum distillation and secondary oil refining processes, oxidation of heavy hydrocarbon raw materials with air oxygen. In recent years, there have been works aimed at obtaining non-oxidized bitumens by compounding heavy oil residues with natural asphaltites [4, 5], which are a product of natural oxidation, as well as studies on the effect of microwave radiation on the quality of oil...
residues and natural bitumens [6, 7, 8]. Despite the certain prospects of these technologies, the scientific aspects of the impact of these processes on the quality of bituminous binders are not fully developed.

The optimal method for obtaining high-quality bituminous binders for various purposes from substandard hydrocarbon raw materials variable in composition and properties is their oxidation with air oxygen [9]. By composition, ultra-viscous oils and natural bitumens are most suitable for producing bituminous binders containing a large amount of resinous-asphaltene substances. The amount of resinous-asphaltene substances in bitumen, solid paraffin hydrocarbons and their composition determine the structural and mechanical parameters: viscosity, penetration, extensibility, softening point, brittleness point, adhesion. The study of the regularities between the composition of the oxidation products of ultra-viscous oil and the physicochemical properties of the oxidation conditions is relevant [10].

2. Methodology

A heavy residue of atmospheric vacuum distillation of Ashalchinsky oil with a boiling point above 480°C was studied as an oxidation feedstock. Oxidation of the oil residue was carried out at a temperature of 255°C and an air flow rate of 0.5 cm³/min, on a laboratory installation of periodic action.

3. Results and Discussions

According to experimental data, the dependences of the oxidation products properties on the process time are constructed as shown in Figure 1.

![Figure 1. Dependence of component composition and viscosity of heavy oil residues of Ashalchinsky oil on time of oxidation](image)

Analyzing the data obtained, let's assume that the more asphaltene aggregates in oxidized bitumen are, the higher their softening point is, including their content will also change the structure of the bitumen: sol, sol-gel, gel structures. Bitumens with a high content of asphaltenes have a gel structure and their softening point is the highest [10]. If the content of asphaltenes and their aggregates increases in the group composition of bitumen, the gel-like structure of the oil dispersion system becomes more rigid, and the brittleness point increases. The component composition of the oxidation products affects the brittleness point and the depth of needle penetration. Oil fractions, resins and paraffins make a special contribution [11, 12]. The brittleness point depends on the state of the dispersion medium. The depth of needle penetration depends on the rheological properties of the bitumen. The dependence between the dynamic viscosity and the component composition of the oxidation products allows us to consider the formation of resins and asphaltenes with a simultaneous increase in the viscosity of samples [13]. The results obtained allow us to draw the following conclusions: at the oxidation time of the heavy oil residue
of 2 and 4.5 hours at the softening point of 45 and 64°C, the value of the depth of needle penetration was at 25°C, from 54 to 590.1 mm, and the extensibility from 62 to 67 cm, and from 54 to 60 cm, respectively as shown in Figure 2.

Figure 2. Physicochemical properties of heavy petroleum residues of Ashalchinsky oil from time of oxidation

The composition of oils and resins, physicochemical properties of oxidation products of heavy oil residue were also studied as shown in Figure 3 and 4.

Figure 3. Dependence of composition of oil fractions and heavy oil residues of Ashalchinsky oil on time of oxidation

Figure 4. Dependence of resins composition of heavy oil residues of Ashalchinsky oil on time of oxidation
After three hours of exposure to oxygen, there is an inverse dependence of the softening point and ductility on the content of polycyclic aromatics. As the number of oils decreases, the brittleness point increases, which is largely determined by the alkane structures in the composition of oil hydrocarbons, and the content of resins, primarily alcohol-benzene, increases. Thus, the performance properties of bitumens are affected by the presence of alcohol-benzene fragments in resin hydrocarbons.

After two hours of oxidation, there is an increase in the extensibility and softening point due to an increase in the concentration of alcohol-benzene resins, which subsequently remains unchanged. During this time, the number of asphaltenes is almost constant. With an increase in their number up to 10%, they begin to affect the properties of bitumen, reduce the indicators of extensibility, penetration, and increase the brittleness and softening points. Further oxidation for 4-5 hours leads to changes in the colloid structure of the oil dispersion system of bitumen. The softening point is inversely proportional to the ratio of paraffin-naphthenic hydrocarbons of oils to asphaltenes. The brittleness point is not affected by oils and resins, as well as the depth of needle penetration. For them, the ratio of polycyclic aromatic hydrocarbons to asphaltenes is of great importance. It should also be noted that as the oxidation time increases, the penetration of the final product decreases, and the softening point increases. Change in the values of extensibility: first increases and then decreases, it is likely due to changes in the concentration of monocyclic and bicyclic aromatic hydrocarbons, and their relationship to the sum of oils and resins.

Under the influence of air oxygen, the amount of oil in the final product of oxidation of the oil residue decreases, and with it the value of the depth of needle penetration decreases, the content of mono- and bi-cyclic aromatics, resins and asphaltenes increase. At the same time, concentrations of paraffin-naphthenic and polycyclic aromatic hydrocarbons decrease, which indicates simultaneous reactions of decomposition of polycyclic aromatics and their formation, followed by condensation into resins and asphaltenes. Thus, the concentration of asphaltenes increases due to the transition of aromatic hydrocarbons to resins, and then to asphaltenes.

Based on the results of liquid-adsorption chromatography in the first six hours of oxidation, the process goes mainly in the direction of accumulation of resins due to the oxidation of oils, so that only the eighth hour increases the relative content of asphaltenes. However, the actual scheme of proceeding reactions can be much more complicated, for example, alcohol-benzene resins under high-temperature oxidation conditions can break down into fragments corresponding to light aromatic hydrocarbons. Judgments about the direction of conversion of hydrocarbons of ultra-viscous oils in the process of their oxidation, as the transition of low-molecular to high-molecular compounds, requires some clarification: under certain experimental conditions, it is possible to break up high-molecular to low-molecular compounds with their subsequent conversion back to heavier components, i.e., cyclic processes of hydrocarbons conversion occur.

A copolymer of ethylene and vinyl acetate with manganese oxide during the oxidation of heavy residual raw materials can influence the composition of the dispersion medium and rearrange the dispersion structure of the final product, changing its physicochemical properties [14-16]. Introduction of paraffin-naphthenic and naphthen-aromatic additives, ethylene copolymer and manganese oxide into the composition of heavy oil residues is reflected in the rate of oxidation [17]. Evaluation of the oxidation kinetics of residual petroleum raw materials was carried out by studying the dependence of the softening point of the final products on the time of the process. To determine the rate constant of reactions that accompany the process of oxidation of residual oil raw materials in the presence of selected additives, the formula of D.C. Lockwood was used: $k_0 = \frac{1}{\tau} \times \ln(t/t_0)$, where $t$ is the softening point of the final product during oxidation, $\tau$ is the softening point of the raw materials [18-21]. The dependence of the tar oxidation rate constants on the process time are shown in Figure 5.
Figure 5. Dependence of softening points and rate constants of final products of heavy oil residue oxidation of a) paraffin-naphthenic and b) naphten-aromatic base

Analysis of the dependence of the softening points of the final products on the duration of heavy oil residues oxidation indicates a multi-stage process, the intensity of which slows down when the softening point of the final product reaches 45°C. It was also observed that the oxidation rate at the second stage is 2 times higher than at the initial stage. The stage character of oxidation of heavy oil residues is also observed with manganese oxide, their transition point is significantly shifted towards small values of the oxidation time. The observed staging of the oxidation process is in agreement with the literature. However, the dependence of the softening points of bitumen samples obtained by oxidation of a heavy oil residue of paraffin-naphthenic base on the duration of the process does not change significantly. This phenomenon can be explained by the high content of solid paraffins and paraffin-naphthenic hydrocarbons in the raw material, which are difficult to oxidize. According to the obtained experimental data it follows that the most intense oxidation proceeds in the presence of manganese oxide. On the contrary, the introduction of ethylene copolymer with vinyl acetate into the raw material reduces the rate of its oxidation. An increase in the duration of oxidation of tar with manganese oxide and ethylene copolymer with vinyl acetate is accompanied by an increase in the softening point and a decrease in the rate constants of the oxidation reaction (Figure 5). These data indicate a decrease in the effectiveness of exposure of air oxygen to raw materials containing polymer, which is associated with an increase in the viscosity of the raw material during the oxidation process. At the final stage of the process, the oxidation reaction constants change less dynamically, this is due to the fact that the reactions accompanied by the formation of asphaltene resins proceed with lower reaction rates compared to polycondensation reactions. Oxidation of petroleum residual raw materials in the presence of ethylene copolymer with vinyl acetate is less intense. Consideration of the dependence of the efficiency of the oxidation process on the (accelerating action) content of additives in the residual high-boiling oil raw materials has shown that the combined additive consisting of a copolymer and manganese oxide is the most effective, the rate constants of the oxidation process on the average increased by 2.5 and 1.5 times.
4. Conclusions

The obtained data on the regularity of changes in the basic physicochemical properties of the final oxidation products from their composition, depending on the duration of the process, allow us to regulate the structure of bituminous materials of a desired quality.

Acknowledgments

The work is performed according to the Russian Government Program of Competitive Growth of Kazan Federal University and for the state assignment in the sphere of scientific activities.

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