

ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
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Improvement of bitumen characteristics during oxidation and modification of
heavy oil residues

The relevance of the topic. Due to the growing consumption of oil and petroleum products, the gradual depletion of oil fields, heavy oil residues (HOR) are becoming in demand in the economy of our country. It is known that up to 30% of HOR are obtained during oil refining: cracking residue, resinous extract, vacuum residue, fuel oil. Today, the problem of creating processes for the economic conversion of heavy residues and improving their quality is acute in oil refining. The complexity of the HOR composition necessitates the search for new ways of their processing. A rational way of processing HOR is their oxidation to obtain oil bitumen.

Current trends in the development of the oil industry, aimed at increasing the depth of oil refining, have a negative impact on the properties of HOR as a raw material for the production of bitumen. This is due to the fact that the quality indicators of bitumen depend on the group and structural composition of the raw material. In addition, the production of bitumens with improved adhesion and high resistance to aging is possible with the oxidation of raw materials at low temperatures, but this leads to a decrease in the productivity of installations.

Improving the production technology through the reconstruction of installations is associated with significant material costs and increase the cost of bitumen. In this regard, the method of influencing the raw materials with modifying additives seems to be available. The introduction of modifiers into raw materials has a positive effect on the properties of bitumen: plasticity, group and structural composition are improved. When deciding whether the use of new modifiers is promising, the main criteria are a high oxidation rate, energy efficiency, and rational resource consumption. Therefore, from a scientific and practical point of view, it is important to investigate the effect of modifiers on the composition and properties of products of liquid-phase oxidation of vacuum residue.

When deciding on the prospects of using new modifiers in the process of oxidation of oil tar, the main criteria are high oxidation rate, energy efficiency and rational resource consumption in conditions of environmental safety. Therefore, both from a scientific and practical point of view, it is important to investigate the effect of modifiers on the composition and properties of products of liquid-phase oxidation of oil tar. Data on the physico-mechanical characteristics of the oxidation products of modified tar are necessary for the development of an optimal mode of the chemical process.

In connection with the above, the work is devoted to the study of the physical, mechanical and rheological characteristics of the products of oxidation of vacuum

residue with the addition of crumb rubber, modification of bitumen with organosilicon additives.

The aim of the work is to study the effect of new modifiers on the process of obtaining oxidized bitumen and improving the characteristics of bitumen.

Research objectives. To achieve this goal, the following tasks were solved:

- study of the composition and physico-chemical properties of the objects of study – vacuum residues of the Pavlodar petrochemical plant (PPCP) and “Asphaltobeton 1” LLP (“AB 1” LLP), crumb rubber;
- study of the effect of rubber crumb on the process of oxidation of vacuum residues and the establishment of optimal process parameters;
- determination of physical, mechanical and rheological characteristics of the products of oxidation of vacuum residues with the addition of crumb rubber;
- study of the effect of crumb rubber on the chemical composition of vacuum residues oxidation products;
- production of asphalt concrete mixtures based on rubber-bitumen binders (RBB) and their pilot testing;
- functionalization of nanosilica and study of its influence on the properties of petroleum bitumen.

Research methods. The following modern instruments and equipment were used for research: FTIR Satellite (Mattson, USA) and Spectrum 100 (PerkinElmer) IR spectrometers, SR5000 (Rheometrics, USA) and Smart Pave 102 (Anton Paar GmbH) rheometers, FEI Quanta 400 scanning electron microscope (Hillsborough, USA), Leica DM 6000M optical microscope, PYRIS 6 TGA thermogravimetric analyzer (Perkin Elmer), Gradient-M and Agilent 7890A/5975C chromatographs, JNM-ECA Jeol 400 ¹H and ¹³C NMR spectrometer (Japan).

The objects of research are HOR – vacuum residues of the PPCP and “AB 1” LLP. Rubber crumb of “Q-Recycling” LLP and nanosilica were used as modifiers for bitumen and bituminous raw materials.

The subject of research is the processes of oxidation of vacuum residues with the addition of crumb rubber, the modification of bitumen with functionalized nanosilica.

The main provisions submitted for protection:

- oxidation of the PPCP vacuum residue at 260 °C for 3 h with the addition of 10 wt.% of rubber crumb with particle size up to 0.6 mm makes it possible to obtain the RBB 90/130 brand with increased extensibility values (80-100 cm), while the duration of vacuum residue oxidation is reduced 2-2.5 times, the curves of elastic modulus and losses are shifted by 5 and 20 °C;
- preliminary mixing of the «AB 1» LLP vacuum residue at 180 °C with 2 wt.% rubber crumb for 0.5 h, oxidation at 260 °C for 2 h and subsequent mixing with 8 wt.% rubber crumb for 0.5 h allows to obtain the RBB 60/90 brand with increased elasticity values (60 °C) and a low brittleness temperature (-23 °C), while the time for obtaining a RBB is reduced 2.5 times;
- RBB obtained by oxidation of the «AB 1» LLP vacuum residue with preliminary modification with rubber crumb have high values of the complex shear modulus and low values of the phase angle after short- and long-term aging,

increased values of the parameters of resistance to rutting and fatigue, stiffness and relaxation rate, which shows their higher resistance to plastic deformation, fatigue cracking and low-temperature (up to $-35\text{ }^{\circ}\text{C}$) cracking;

- vacuum residue oxidation products with the addition of rubber crumb are characterized by an increased content of aromatic hydrocarbons, H atoms in the composition of olefin groups and bound in the α -position with aromatic and carbonyl carbon atoms, heteroatoms, quaternary C atoms and a reduced content of paraffins and cycloparaffins, methyl group atoms associated with methylene and methine group or aromatic ring;

- modification of bitumen grade PG 50/70 1 wt.% by silica particles functionalized by amine and alkyl groups $\text{C}_{14}\text{N@SNP-3}$ leads to a shift of the elastic modulus curves by $7\text{-}8\text{ }^{\circ}\text{C}$, which confirms the improvement of viscoelastic properties of bitumen.

The main results of the study:

1. Oxidation of the PPCP vacuum residue was carried out at $240\text{-}260\text{ }^{\circ}\text{C}$ for 2-3 h with the addition of 1-10 wt.% of rubber crumb. An increase in the oxidation temperature led to a decrease in penetration, an increase in the softening temperature and the extensibility of the oxidation products. With an increase in the content of rubber crumbs up to 7-10 wt.% physico-mechanical properties of RBB are increasing. To obtain the RBB 90/130 brand, the optimal conditions are: $260\text{ }^{\circ}\text{C}$, 3 h, 10 wt. % of rubber crumb. The addition of rubber crumb led to a shift in the curves of elastic modulus and losses to the region of positive temperatures, which contributes to their resistance to deformation effects.
2. The «AB 1» LLP vacuum residue was oxidized at $240\text{-}260\text{ }^{\circ}\text{C}$ under different technological conditions (time 2-7 h, mixing before and after oxidation) and modified with 5-15 wt. % of rubber crumb with size 0.6-1.0 mm and less than 0.6 mm. Preliminary mixing of raw material with a modifier at $180\text{ }^{\circ}\text{C}$ for 0.5-1 h led to a sharp decrease in penetration and an increase in the softening temperature of oxidation products. Mixing of «AB 1» LLP vacuum residue with 2 wt. % rubber crumb at $180\text{ }^{\circ}\text{C}$ for 0.5 h, oxidation at $260\text{ }^{\circ}\text{C}$ for 2 h, subsequent mixing of the product with 8 wt. % rubber crumb for 0.5 h allowed to obtain the RBB 60/90 brand with an increased elasticity value ($60\text{ }^{\circ}\text{C}$) and a low brittleness temperature value ($-23\text{ }^{\circ}\text{C}$).
3. The product of «AB 1» LLP vacuum residue modified with rubber crumb has increased values of the complex shear modulus, low values of the phase angle, high values of the parameters of rutting and fatigue after short- and long-term aging, which confirms the rigidity and resistance to plastic deformation and fatigue cracking of bitumen.
4. According to the results of chromatographic analysis with mass spectrometric detection and IR spectroscopic analysis, the products of oxidation of «AB 1» LLP vacuum residue with the addition of rubber crumb are characterized by an increased content of aromatic hydrocarbons and a reduced content of alkanes and cycloalkanes. NMR spectroscopic analysis of the samples showed an increase in the content of H atoms of olefin groups and in the α -position to aromatic and carbonyl carbons, heteroatoms, a decrease in the number of C atoms of methyl

groups associated with methylene, methine groups or aromatic ring and an increase in the number of quaternary aliphatic C atoms. These data indicate a decrease in the content of oils and an increase in the content of resins and asphaltenes, which consist of condensed aromatic structures.

5. Modification of bitumen grade PG 50/70 1 wt.% by silica particles functionalized by amine and alkyl groups C₁₄N@SNP-3 led to a shift of the elastic modulus curves to the region of elevated temperatures by 7-8 °C, which confirms the improvement of viscoelastic properties of bitumen.
6. On the basis of RBB obtained by oxidation of «AB 1» LLP vacuum residue, modified with rubber crumb, 123 tons of an experimental batch of asphalt concrete mixture of type B were prepared and an experimental road section with a width of 12 m and a total length of 80 m was laid on the Almaty highway at 53 Burunday street (towards Kusainuly street). The acts of production of the experimental batch and laying of asphalt concrete mixture using oxidized bitumen modified with rubber crumb were obtained. Recommendations for the production technology of oxidized modified bitumen have been prepared.

Substantiation of the novelty and importance of the results obtained:

- a new method for obtaining oxidized modified bitumen by oxidation of PPCP and «AB 1» LLP vacuum residues with the addition of rubber crumb has been developed;

- optimal modes of vacuum residue oxidation processes with preliminary and subsequent mixing with rubber crumb have been established to obtain RBB according to physico-mechanical parameters that meet the requirements of ST RK 2028-2010;

- for the first time, viscoelastic and mechanical characteristics of vacuum residue oxidation products with the addition of rubber crumb have been established to determine resistance to deformation and destruction;

- a change in the hydrocarbon composition of vacuum residue after oxidation with the addition of rubber crumb has been established to explain its effect on the properties of the obtained bitumen;

- the effect of silica particles modified with amine and alkyl groups on the viscoelastic characteristics of bitumen has been established for the first time;

- a pilot industrial test of RBB and asphalt concrete mixture based on them was carried out with the laying of an experimental section of the road coating.

The theoretical significance of the work is to establish the regularities of changes in the physical and mechanical characteristics of bitumen obtained by oxidation of vacuum residue during preliminary mixing with rubber crumb. The practical significance of the research is to improve the physical and mechanical characteristics of petroleum bitumen by modifying and oxidizing bitumen raw material.

Compliance with the directions of scientific development or state programs. The work was carried out within the framework of the theme «Development and implementation of technology for the production of oxidized modified bitumen» of the Scientific technical program «Work on road management in terms of improving the regulatory and technical base», funded by the RSE on

PEM «National Center for Quality of Road Assets» of the Ministry of Industry and Infrastructure Development of the Republic of Kazakhstan. Contract No. 190540022580/210848/00 dated May 6, 2021.

Publications. 13 publications have been published, including 3 articles in international publications indexed in the Web of Science and Scopus databases, 3 articles in republican journals from the List of recommended publications, patent for a method for obtaining bitumen binder, 5 reports in conference materials.

Personal contribution of the doctoral student to the preparation of each publication:

1. Article «Aging Process Effects on the Characteristics of Vacuum Residue Oxidation Products with the Addition of Crumb Rubber» in the journal «Molecules»: preparation of a review and analysis of literature data, obtaining and processing results.

2. Article «Functionalization and Modification of Bitumen by Silica Nanoparticles» in the journal «Applied Sciences»: preparation of a review and analysis of literary sources, obtaining and processing of analysis results at the University of Calabria.

3. Article «Oxidation of Vacuum Residue with the Addition of Crumb Rubber» in the journal «Eurasian Chemical-Technological Journal»: obtaining and discussing experimental data, preparing a review of literature data.

4. Article «Oxidation of heavy oil residues in the presence of catalysts and modifiers» in the journal «Combustion and Plasmochemistry»: preparation of a review and analysis of literary sources.

5. Article «Functionalization and modification of bitumen by silica particles» in the journal «Industry of Kazakhstan»: preparation of a review and analysis of literary sources.

6. Article «Improvement of physical and mechanical characteristics of bitumen and asphalt concrete mixtures by modification of rubber crumb» in the journal «Bulletin of EKTU»: obtaining and discussion of experimental data.

7. Patent for the «Method of obtaining bitumen binder» search and analysis of analogues and prototype, obtaining experimental data.

8. Materials of reports of scientific conferences and symposia: description and presentation of experimental data and analysis results.

The structure and scope of the dissertation. The dissertation consists of an introduction, 4 chapters, conclusion and appendices. The work is presented on 160 pages of text, contains 18 tables, 59 figures and 3 appendices. The list of sources used includes 122 titles.