

## ANNOTATION

of the dissertation work of Ainabekov Nurzhan Bauyrzhanovich on the topic: “Regulation of structural transformations in the processes of production of modified bitumen materials from oil residues from Kazakhstani deposits” submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D07170 – “Chemical technology of organic substances”

Due to a number of valuable operational properties and increasing scale of production, petroleum bitumen is one of the most widely used petroleum products in the construction industry, especially in road construction. It is used for construction and repair of road and airfield surfaces, industrial building floor bases, soil stabilization, protection of metal and concrete from corrosion, production of roofing, hydro-, heat- and vapor-insulating coatings and materials, protection from radioactive radiation, in the production of paints and varnishes, etc.

The demand for high-quality petroleum bitumen tends to grow. The requirements for the quality of the produced petroleum bitumen, imposed by consumers of this type of product, are also increasing.

Due to the fact that bitumen has long been considered in our country not a target, but a by-product of oil refining, most of the bitumen produced in the Republic of Kazakhstan does not meet the requirements of technical standards. In addition, the ever-increasing demands on the quality and performance characteristics of bitumen-based materials can no longer be met solely by selecting raw materials and improving bitumen production technology.

Significant improvement of bitumen properties can be achieved by introducing fillers, surfactants and various modifiers, in particular, polymers and their waste, into their composition, i.e. obtaining bitumen-polymer compositions. Modification of bitumen with polymers allows increasing heat, frost, weather resistance and resistance to aggressive environments, plasticity and elasticity of compositions.

Research aimed at studying new local raw material sources for the production of high-quality road bitumen, development and study of the basic principles and patterns in the preparation of raw materials for bitumen production and in the process of its oxidation, as well as in the production of commercial products, based on a scientific approach to the selection and use of modifying additives and components to bitumen are a very relevant topic.

In most cases, polymers are used as bitumen modifiers. The cost price of such polymer-modified bitumens is quite high. Therefore, the issue of reducing the cost price of the binder by including cheaper additives in the composition of bitumen compositions, which can be obtained on the basis of various man-made waste, is relevant.

**The aim of the study** is to regulate structural transformations in raw materials and products of production of oxidized and modified bitumen materials that meet modern quality requirements from the remains of some oils of Kazakhstan fields.

### **Tasks of the research:**

- study of characteristics of some heavy oil residues of different selection depths obtained during distillation of heavy high-resin oil of Western Kazakhstan and

assessment of possibilities of their use for production of high-quality road bitumen;

- study of group chemical composition of raw materials and its influence on results of bitumen oxidation process and main quality indicators of obtained bitumen;
- justification of choice of oil residues most suitable for production of high-quality road bitumen;
- development of laboratory samples of oxidized bitumen - bases for modification corresponding to grades BND 90/130; BND 70/100; BND 50/70;
- study of structure of modified bitumen and establishment of mechanism of interaction of selected additives with bitumen binder;
- selection of technology of combining bitumen with destructible rubber waste and study of processes of production of polymer-rubber-containing bitumen binders.

**Methods and objects of the research.** The methodology of the study consisted of a systematic study of the physical and chemical properties, detailed fractional and chemical compositions of the original tars and bitumens obtained on their basis and is based on fundamental and experimental achievements in the field of processing heavy oil residues and oil dispersed systems. In the work for studying the properties of raw materials of bitumen production, bitumen materials and bitumen-polymer compositions, standard methods were used to determine the softening point on the device “Ring and Ball” according to GOST 11506, brittleness temperature according to GOST 11507-78, penetration according to GOST 11501, ductility according to GOST 11505. In the performance of the work, modern physicochemical methods of research and analysis of the initial and final products were applied: IR Fourier spectroscopy (Shimadzu JR Prestige-21) and low-vacuum scanning electron microscopy (JEOL JSM-6490 LA). In processing the results of experimental studies, methods of mathematical modeling and statistical data processing were used.

The objects of the research are: oil from the Kalamkas field; the remains of this oil boiling above 380, 400, 420°C; tire reclaim from tire crumb; bitumen modifier - a copolymer of ethylene with butyl acrylate and glycidyl methacrylate (EBG); rubber crumb with dimensions of 0.6-1.0 mm; technical carbon (obtained by recycling old tires using the pyrolysis method) “ECO-Shina” LLP.

**The main provisions submitted for defense:**

- a set of new data on changes in the structural-group composition of bitumen from the remains of heavy oils of Kazakhstan;
- results of experimental studies of the dependencies of the physicochemical properties of road bitumen on the depth of selection of distillate fractions of heavy high-resin Kalamkas oil;
- rational compositions of modified bitumen and polymer-bitumen binders;
- results of bitumen modification with tire reclaim;
- results of bitumen modification with technical carbon from worn tires;
- mathematical model of bitumen production modified with polymer additives;
- main economic indicators of bitumen material production modified with technical carbon by “ECO-Shina” LLP.

### **Main results of the research:**

- optimal technical requirements for raw materials based on residues from the processing of Kalamkas oil, intended for the production of high-quality road bitumen, were determined;
- technological solutions for obtaining combined polymer-containing additives, their optimal concentrations for modifying the properties of bitumen in order to ensure their required quality;
- establishing the maximum possible introduction of carbon black from worn tires into bitumen grade BND 50/70 less (4% by weight). It is possible to introduce carbon black from worn tires into bitumen grade BND 70/100 up to 5% by weight;
- pilot tests of bitumen grades BND70/100 and BND 50/70 modified with carbon black by “ECO-Shina” LLP at “Neftekhimstroy-Yug” LLP;
- technology for obtaining modified bitumen, which is confirmed by patents of the Republic of Kazakhstan for utility model (No. 9179; and No. 9497);
- results of preliminary technical and economic calculations, which show that the economic efficiency of production of bitumen materials modified with technical carbon from worn-out tires of “ECO-Shina” LLP is 34 334 136 tenge per year.

### **Justification of the novelty and importance of the obtained results:**

- it was established that oxidized bitumens obtained from the vacuum residue of Kalamkas oil, boiling at a temperature above 380 and 400°C, correspond to petroleum road bitumen grade BND 70/100 according to STRK1373 - 2013. Residues from atmospheric-vacuum distillation of heavy oil from the Kalamkas field are recommended as an independent raw material, a component of raw materials in the production of oxidized road bitumens or a basis for obtaining modified bitumens at enterprises of the Republic of Kazakhstan;

- a relationship was established between the group composition and quality indicators of residual and oxidized bitumens obtained from various residues of Kalamkas oil. With the increase of resins and asphaltenes in the residues (17.4/7.7 at 380°C; 19.6/9.8 at 400°C; 22.5/12.4 at 420°C), the density increases (964.0 kg/m<sup>3</sup> at 380°C; 969.2 kg/m<sup>3</sup> at 400°C; 975.8 kg/m<sup>3</sup> at 420°C), the total sulfur content (1.82% by weight at 380°C; 1.97% by weight at 400°C; 2.06% by weight at 420°C), Conradson coking index (8.5% at 380°C; 10.3% at 400°C; 11.4% at 420°C), flash point (214°C at 380°C; 219°C at 400°C; 228°C at 420°C) and conditional viscosity at 80°C (8.6 sec. at 380°C; 16.8 sec. at 400°C; 20.2 at 420°C).

- it was established that the optimal bitumen-reclaimed composition (with a tire reclaim content of 20%) is superior in a set of properties to bitumen modified with an optimal content of EBG (1.6%). The technology of modifying bitumen with reclaim is less time-consuming, more economically advantageous and environmentally efficient, since it utilizes multi-ton waste from worn tires;

- the possibility of using carbon black from worn tires as a modifier for petroleum bitumen was established. A rational amount of additive should be considered to be 4% of carbon black from worn tires for BND50/70, and up to 5% for BND70/100;

- a chemical method of rubber devulcanization for bitumen modification is proposed, in which devulcanization occurs directly in the bitumen environment. In this case, the main goal is achieved - bitumen modification with linear rubber. Compounds

consisting of DBU and TFF (1,8-diazabicyclo[5.4.0]undec-7-ene and a compatibilizer) in a weight ratio of 1:1 are used as devulcanizing agents. The compatibilizer is a petroleum distillation product with a boiling point above 240°C.

The theoretical and practical significance of the work lies in substantiating the change in the group chemical composition of tars during oxidation at different durations. Optimal technical requirements for raw materials based on the residues of Kalamkas oil processing intended for obtaining high-quality road grade bitumen have been determined. The working range of the conditional viscosity of raw materials at 80°C has been established, which is 8.6-16.8 s.;

This work is of practical importance in optimizing the formulation of raw materials for bitumen production and in the process of its oxidation, as well as in the production of commercial products, to obtain petroleum bitumen materials with quality that meets modern consumer requirements. The efficiency of using carbon black from worn tires as modifying additives is evidenced by the results of field tests, where it was found that the introduction of carbon black from worn tires has a different effect on different bitumens: it reduces the softening temperature, improves the elasticity of the bitumen binder, reduces penetration based on BND70/100 bitumen, and increases it based on BND50/70 bitumen, which leads to a change in the grade of the original bitumen, and also improves an important indicator of low-temperature properties – the brittleness temperature. The recommended rational amount of additive is 4% of carbon black from worn tires for BND 50/70, and up to 5% for BND 70/100. (test report of BND70/100 and BND 50/70 bitumen grades at the “Neftekhimstroy-Yug” LLP enterprise. No. 99, May 31, 2024). The results of the work have also been implemented in the educational process in the discipline “Modern and promising thermolytic processes of oil refining” (report No. 89 dated May 29, 2024). Based on the research results, 2 patents of RK for utility models were obtained No. 9179; and No. 9497.

**Compliance with scientific development directions or state programs.** The dissertation work was completed at the Department of Inorganic and Petrochemical Production Technology at “M. Auezov South Kazakhstan University” NCJSC, Research Laboratory of Petrochemistry and Composite Polymer Materials within the framework of the state budget scientific research work B-21-03-03: on the topic of “Development of new technologies and processes for processing hydrocarbon raw materials of the Republic of Kazakhstan to obtain motor fuels and special-purpose products with improved performance properties”. The scientific data of the dissertation are based on the results obtained through experimental work and physical and chemical studies using modern research equipment and devices. Works related to mathematical modeling and data processing were performed using the MatLab programming environment.

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

On the topic of the dissertation, 13 scientific works were published, including: 1 article in international scientific publications included in the Scopus database, 3 articles in publications recommended by the authorized body, 7 articles in proceedings of international and national conferences, 2 patents of the Republic of Kazakhstan for a utility model.

1. Article “Bituminous modified materials from Kazakhstani oil field” in the journal *Advances in Polymer Technology* - review preparation and data analysis, obtaining and processing the results.

2. Article “Selection of raw materials for obtaining bitumen materials based on local resources” in the journal “*News of NAS RK*” - review preparation and literature data analysis, obtaining and processing the results.

3. Article “Influence of group chemical composition of highly viscous oil residues on the quality of petroleum road bitumens” in the journal “*Oil and gas*” - review preparation and literature analysis.

4. Article “Use of carbon black as a modifier for petroleum bitumen” in the journal “*Oil and gas*” - obtaining and discussion of experimental data.

5. Article “Production of modified bitumen materials” in the proceedings of the 25<sup>th</sup> International scientific and practical conference of students and young scientists on the topic “Chemical technology and biotechnology of the 21<sup>st</sup> century” dedicated to the 30<sup>th</sup> Anniversary of Independence Day of Kazakhstan, as well as the 180<sup>th</sup> Anniversary of Ybyrai Altynsarin, 110<sup>th</sup> Anniversary of Batyrbek Birimzhanov - preparation of a review and analysis of literary sources.

6. Article “Possibilities of regulating structural transformations using sulfur - bypassed oil product” in the Proceedings of International Conference ICITE-2021 - preparation of a review of literary sources.

7. Article “Road bitumen from Kazakhstan oils” in the collection of Science Week of SPbGMTU-2021: collection of reports of the All-Russian Science Festival “*Nauka 0+*” - preparation of a review of literary data.

8. Article “The importance of regulating the properties of raw materials on the efficiency of production technologies for obtaining bitumen” in the collection of works of the Scientific and Technical Conference “Actual problems of marine energy” - search and analysis of analogues, preparation of a review of literary sources.

9. Article “Scientific and technological foundations for modifying the properties of bitumen materials” in the collection Science Week of SPbGMTU-2022: collection of reports of the All-Russian Science Festival “*Nauka 0+*” - search and analysis of analogs, preparation of a review of literary sources.

10. Article “Study of the destruction of the regenerate in the process of bitumen modification” in the proceedings of the Scientific and Practical Conference “Modern Trends in Higher Education and Science in the Field of Chemistry and Chemical Engineering”, dedicated to the 90<sup>th</sup> anniversary of the birth of Academician of the NAS RK E.M. Shaikhutdinov - obtaining and discussing experimental data, searching and analyzing analogs and a prototype.

11. Article “Application of modified bitumen materials from Kazakhstan deposits” in the Proceedings of the Scientific and Technical Conference “Innovative technologies and current problems of the food, chemical and oil and gas industries” - obtaining and discussing experimental data.

12. Ainabekov N.B., Sagitova G.F. Method for producing modified bitumen. Patent for utility model No. 9197 RK, 2024.

13. Ainabekov N.B., Sagitova G.F. Method for producing modified bitumen. Patent for utility model No. 9497 RK, 2024.

**Structure and volume of the dissertation.** The dissertation work is presented on 117 pages of computer text, includes 18 tables and 40 figures. The dissertation work consists of an introduction, 4 chapters, a conclusion, a list of 170 references and appendices.