ANNOTATION

for the dissertation for the degree «Doctor of Philosophy» (PhD) in specialty

8D07102 – «Chemical technology of organic substances»

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DEVELOPMENT OF MODIFIED BITUMEN-MINERAL COMPOSITIONS

Relevance of the research topic. The problem of creating effective road surfaces is relevant from the point of view of resource conservation, ensuring reliability, and durability of their performance characteristics. Due to the chemical nature and structural features of asphalt concrete, the main way to increase the service life of coatings is to change the structure and properties of organic binders. Widely used as organic binders, road bitumen is not able to provide the required physical and mechanical properties of coatings and their durability in modern conditions. Modification of road bitumen, as evidenced by the experience of world practice, is characterized by diversity, branching ways of its technological implementation, the essence of which is reduced to two main areas. One of the technological directions for improving the quality of bitumen is based on the introduction of surfactant modifiers. Most often, cationic surfactants are used to ensure high adhesion between bitumen and the mineral component of the road surface. Another direction is based on the modification of bitumen with polymer materials, which give their characteristic physical and mechanical properties to the binder, by creating a spatial structural grid in bitumen. However, a significant increase in the cost of modified bitumen binders is a deterrent to their use.

A promising direction for creating a bitumen binder that meets the most modern world requirements is the joint introduction of effective surfactants (from the nomenclature of industrial and synthesized) and polymers (spent and requiring recycling). However, their application is complicated by the fact that the generation of the specified surface properties and microstructure of bitumen is carried out not by chemical means, but by transformations implemented at the level of intermolecular interactions. The narrow range of energy values within which various states of easily transformable modified forms are realized requires targeted selection and optimal dosage of additives to achieve the desired effect and avoid undesirable side effects.

Compliance with areas of scientific development or state programs. The dissertation work was carried out in accordance with the plan of research works within the framework of grant financing programs for scientific and scientific-technical projects of the Ministry of Science and Higher Education of the Republic of Kazakhstan for 2023-2025 in

priority areas of science development, AP19677707 «Development of modified asphalt concrete compositions using products of secondary processing of industrial waste».

The objects of the study are petroleum road bitumen BND 100/130, AG-4I – refined sealing liquid based on polyisobutylene, AMDOR-10 – industrial adhesive additive, AS-1 – surfactant synthesized from the petrochemical waste.

The subjects of the study are adhesive, hydrophobizing and strength effects of additives in modified bitumen-mineral compositions; optimal formulation recommended for the production of asphalt concrete with an improved complex of performance characteristics.

The purpose of the work is to develop modified bitumen-mineral compositions with an improved set of performance characteristics by optimizing the composition based on the results of physicochemical and physicomechanical studies.

To achieve this goal, the following **tasks were set**:

1. Study of physical and chemical properties of model binary "bitumen-AS-1", "bitumen-AMDOR-10"," bitumen-AG-4I "and triple" bitumen-AG-4I-AS-1 " systems, the individual components of which are petroleum road bitumen, additives based on organic amine derivatives and a spent solution of polyisobutylene in mineral oil (sealing liquid AG-4I);

2. Investigation of the influence of the concentration of additives in bitumen on the wetting processes of mineral fillers of various nature and the hydrophobicity of bitumen films, on the adhesive efficiency of modifiers, as well as on the development of structuring processes in the volume of a dispersed bitumen system;

3. Evaluation of the influence of compositions on the physical and mechanical characteristics of modified bitumen and asphalt-concrete mixtures;

4. Development of the optimal composition of modified bitumen-mineral mixtures with an improved set of physical and mechanical characteristics.

Research methods. Certified chemical and instrumental methods of analysis were used: infrared spectroscopy (Infralume FT-08), atomic force microscopy (Solver Spectrum), determination of surface tension and contact angle on an automatic measurement system of the ACAM series, and viscometric analysis (viscometer VZ-DIN4). The physical and mechanical characteristics of the modified bitumen binder and the strength properties of asphalt concrete based on it were evaluated according to standardized methods using an apparatus for determining the softening temperature of petroleum products (KISH-20), an automatic apparatus for determining the brittleness temperature of petroleum bitumen (ATH-20), an automatic penetrometer (PN-20), and an instrument for determining ductility bitumen (DB-20-100), automatic testing press IP-100-M, methods of mathematical modeling.

A scientific novelty of the dissertation work.

-For the first time, the effectiveness of the combined use of a spent sealing liquid based on polyisobutylene and a surfactant AS-1 synthesized from petrochemical waste as modifiers for road bitumen has been established. The maximum wetting effect of the modified bitumen binder in relation to the surface of the mineral filler is established when two modifiers are combined, localized at different adsorption centers of crushed stone, which leads to a deeper decrease in the specific surface energy and the contact angle of wetting;

- It is proved that the maximum adhesion of bitumen to the mineral component of the road surface is provided in the combined presence of modifiers and reaches a maximum at C_{AG-4I}=1.0 g/dm^3 and C_{AS-1}=1.0 g/dm^3;

- For the first time, a close correlation was revealed in the nature of changes in the dispersed composition of modified bitumen determined by the AFM method and the compressive strength indicators of asphalt concrete samples. The maximum effect of increasing the strength of asphalt concrete (R_{20} by 28.13 % and R_{50} by 63.63%) based on the triple composition " bitumen-AG-4I-AS-1 "(C_{AG-4I}=1.0 g/dm^3; C_{AS-1}=1.0 g/dm^3) was achieved with the lowest the size of asphaltene aggregates of modified bitumen (a_{av}=1.66 microns);

- A correlation was found between the hydrophobizing effect of modifiers in bitumen and the water resistance of modified asphalt concrete. The minimum water saturation of asphalt concrete samples was recorded at the same concentration of modifiers (C=1.0 g /dm^3), at which the maximum contact angle of wetting with water was observed;

- Modifying effects of additives – adhesive, hydrophobizing, strengthening – are systematized in the form of multi-factor dependencies, which are used to establish optimal concentrations of additives in the bitumen binder and predict the performance characteristics of coatings.

Practical significance lies in expanding the range of effective additives and developing a modified bitumen composition based on them, including the combined presence of polymer and surfactant, the effectiveness of which is confirmed by the results of an independent examination in the testing laboratory "National Center for Road Asset Quality" in the North Kazakhstan region. The developed technology of modifying bitumen with polymer and surfactants makes it possible to efficiently dispose of industrial waste by reusing it as modifiers, and eliminates the use of expensive imported adhesive additives in the production of asphalt concrete in the Republic of Kazakhstan.

Dissertation provisions submitted for defense:

- Influence of modifier concentration and temperature on surface tension and structuring processes in binary "bitumen-AS-1", "bitumen-AMDOR-10", "bitumen-AG-4I" and triple "bitumen-AS-1-AG-4I" systems. Dependence of changes in the strength parameters of asphalt concrete samples on the dispersed composition of modified bitumen;

- Influence of the concentration of additives in the bitumen binder on the wetting processes of mineral fillers of various nature and their adhesive efficiency. Modeling of the joint effect of additives on the wetting properties of modified bitumen compositions;

- Dependence of the effect of modifiers on the hydrophobicity of bitumen films. Nomogram of the dependence of the water saturation index of asphalt concrete on the contact angle of water wetting of modified bitumen films;

- Influence of modified bitumen compositions on the physical and mechanical characteristics of the bitumen binder. Optimal composition of the modified asphalt-concrete mixture for the road surfaces, including the combined presence of AG-4I and AS-1.

The validity and reliability of the results and recommendations is based on the use of standard proven research methods using methods of statistical processing of experimental results with a high correlation coefficient.

Approbation of the work. The main content of the dissertation is published in 4 journals included in the Scopus and Web of Science databases, and in 3 journals recommended by the Committee for Quality Assurance in Science and Higher Education of the Ministry of Education and Science of the Republic of Kazakhstan. The main results of the dissertation work were reported and discussed at 5 international symposia and scientific and practical conferences.

The structure and scope of the dissertation. The dissertation consists of an introduction, 5 sections, conclusion, a list of used sources of 217 titles, contains 164 pages of text, 65 figures, 45 tables.

The introduction substantiates the relevance of the topic. It is noted that an effective solution to the problem of improving the physical and mechanical characteristics of asphalt concrete by modifying the bitumen binder is based on expanding the range of additives synthesized on the basis of industrial petrochemical waste and spent polymer materials. The purpose, objectives, object and subject of the study are determined, the scientific novelty and practical significance of the work are revealed, and research methods are presented.

The first section analyzes the reasons for the unsatisfactory quality of asphalt concrete road surfaces, as well as modern directions for modifying bitumen-mineral compositions to

improve their functional characteristics. The expediency of modifying petroleum road bitumen with surfactants and spent polymers is substantiated, which is especially relevant from the point of view of resource conservation. The problems arising in determining the nomenclature of effective modifiers and the possibility of their joint application, associated with the lack of a common physicochemical theory of modifying bitumen compositions, have determined the directions of this research.

The second section includes the study of the surface properties of binary "bitumen-surfactants", "bitumen-polymer" and triple "bitumen-AG-4I-AS-1" modified bitumen compositions depending on the concentration of the modifier and temperature conditions by measuring the surface tension of the modified binder at the interface with air.

The third section presents the results of studies to assess the effect of concentration of modifiers and temperature regimes on structuring processes in binary "bitumen-AS-1", "bitumen-AMDOR-10", "bitumen-AG-4I" and triple "bitumen-AG-4I-AS-1" systems using viscometric analysis and method of atomic force microscopy.

The fourth section presents the results of determining the effect of modifiers on the wetting of mineral fillers of various natures with bitumen and the adhesive effectiveness of additives in a bitumen-mineral composition.

The fifth section considers the establishment of the effect of modifiers on the hydrophobicity of bitumen films in order to achieve minimum water saturation. Correlations between the contact angle of water wetting of modified bitumen films and the water saturation index of asphalt concrete samples are derived, which makes it possible to predict the hydrophobicity of the formed asphalt concrete coatings.

The sixth section presents an analysis of the complex of physicomechanical characteristics of the modified bitumen binder, which allows us to confirm the recommended concentration modes of introducing modifiers into the bitumen binder, established earlier; an optimized composition of the asphalt concrete mixture and a technical and economic assessment are given.

In conclusion, the main results of the conducted complex of experimental studies are presented.

Personal contribution of the author. The author's personal contribution consists in conducting theoretical and experimental studies substantiating the main provisions submitted for defense, and the author also plays a significant role in the generalization and analysis of the results obtained.

Description of the doctoral student's contribution to the preparation of scientific publications. The doctoral student is the corresponding author of all scientific articles published based on the results of research work. The main content and results of the dissertation work are reflected in 12 scientific papers, of which 4 articles are published in scientific journals included in the Scopus and Web of Science databases, 3 articles in republican journals included in the List of scientific publications recommended for publication of the main results of scientific activity, 5 reports in the materials of international conferences and symposia.

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