

Affecting the Improvement of the Quality of Petroleum Bitumen and their Modification

Juraev V. N., Mirkhamitova D. Kh., Jadilova D. A.
Tashkent State Technical University Almalyk branch

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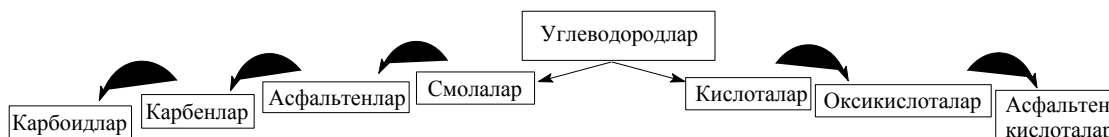
ABSTRACT

Secondary alkanolamines were used as modifiers in the experiments in order to prevent wear and destruction of bitumens and to increase their service life. Taking into account the compounds of sour gases contained in secondary alkanolamines, they were studied because they can be used as structuring process accelerators in the polymer-bitumen composition.

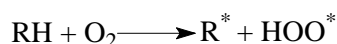
Introduction. Today, the use of polymer-bitumen coatings for covering highways and airfields has increased by 64%. They differ in asphalt-bitumen compositions by their resistance to heat, cold, bending, stretching, friction and dynamic forces. More than 10 natural and synthetic ingredients are used to improve technological, physical-mechanical and dynamic properties of polymer-bitumen compositions. In order to increase the resistance of polymer-bitumen compositions to cold, heat, bending, friction, stretching, and service time, attention is being paid to the creation of ingredients that shape the structure of their technological, physical-mechanical, and dynamic properties based on pre-given requirements [1-3].

Research results. There are methods of physical and chemical modification of domestic petroleum bitumens with elastomers and polymers with high elastic deformation ability at very low temperatures ($-40\text{ }^{\circ}\text{C} \div -60\text{ }^{\circ}\text{C}$) and high temperatures (more than $100\text{ }^{\circ}\text{C}$). Therefore, when polymer-bituminous binders (PBB) and bitumen are modified with additional ingredients, it is possible to ensure their strength by increasing their heat resistance and frost resistance, thereby expanding the temperature range during their operation [4-5]. In this case, it is necessary to focus on the oxidation process, which plays a key role in bitumen extraction technology. The modern technology of oxidized bitumen production consists of oxidation of oil residues with air oxygen without a catalyst: in industrial conditions, the temperature range is $230\text{-}270\text{ }^{\circ}\text{C}$; air flow rate $3.0\text{-}5.7\text{ m}^3/(\text{m}^2 \cdot \text{min})$; the duration of the process is up to 12 hours, and it is carried out in a column with a diameter of 3.2-3.4 m and a height of 14-15 m. 500 mm.sim.u. will be up to The amount of distillation and losses depends on the content of volatile substances in the raw material and the amount of oxidation, in the range of 0.5-10% compared to the raw material. Water vapor and carbon dioxide are released in the system. An exothermic oxidation reaction increases the temperature in the reaction zone. Several reactions occur during oxidation:

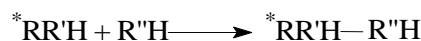
oxidation, dehydrogenation, dealkylation, polymer oxidation, polycondensation, cracking. The main part of the oxygen in the air goes to the formation of water and carbon dioxide, and a small part - to the formation of organic substances containing oxygen [6]. Oil hydrocarbons one at the time two in the direction oxidizes :



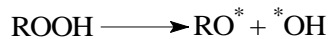
The reaction mechanism of converting raw materials into bitumen goes as follows:



The interaction of the formed radicals with the new hydrocarbon molecule leads to the production of a stable product:



Here goes the process of radical disproportionation. Due to the relatively low concentration of hydrocarbon radicals, their recombination ($2 R^* \rightarrow R-R$), that is, reionization occurs less often, and the interaction of radicals with oxygen is to a lesser extent than with the molecules of the initial substance:



The reaction chain continues as follows :



According to this scheme, asphaltenes can be formed not only from their resins (oxygen-containing compounds), but also directly from aromatic compounds due to radical formation processes. The influence of starting materials on the properties and oxidation kinetics of bitumen is determined to a greater extent by their molar ratio, rather than by the total concentration of tar and asphaltenes. Depending on the value of their molar ratio, the starting substance can be in the form of a solution or in a dispersed system at the temperature of oxidation. In these cases, oxidation processes increase in different ways. Thus, it is proposed to consider oxidation processes in bitumen production as sequential reactions:

The first stage: when the raw material is in the form of a solution under synthesis conditions, its oxidation changes begin with the formation of substances in the form of carbonyl, complex ether and carboxyl groups containing oxygen. Oxygenated of compounds maximum concentration _ _ to the temperature depends and his decrease with significant level increases . With that together their to tars slowly rotation observed . Resins at a given con ts entration e rhythm is dispersed to

the system becomes _ Such of the system dispersed phase oxygenated from compounds tars and asphalt skins _ harvest to be reaction yes _ speed sharp increases . This changes water release of oxygen in the form of formation with condensation reaction mechanism with continues ; _

The second stage: when the mole ratio between asphaltenes and resins is equal to 0.5, strong complexes are formed in the reaction volume [9]. Hard paraffins have a great influence on the properties of bitumen. Their content in raw materials should not exceed 4-5%. Exceeding these values leads to a sharp decrease in the structural and mechanical strength of bitumen. As a result of the excessive hydrocarbon content of domestic petroleum bitumen, the service life of asphalt concrete is 2-3 years. In this case, if the properties of the road surface are influenced, firstly, by the extreme continentality of the republic's weather (50-55 °C in summer and -30--40 °C in winter), the chemical composition of bitumen is the second influencing factor.

The results of the research showed that the reasons for the short service life of bitumens with a high amount of hard paraffin were concluded as follows: in the summer season, under the influence of high temperature, mineral additives (sand, gravel, sheben, etc.) in the coating accelerate the deposition of softened bitumen. Bitumen remains on the surface of the road surface. As a result, by the winter season, the bitumen remaining on the top hardens and cracks due to external influences. Later, due to precipitation, the quality of the road surface deteriorates. The appearance of such defects is related to the complex effects of weather, climate and mechanical factors, but the main factor that determines the destruction of pavements in the operation of highways is the wear of bitumen, which is the binder of asphalt concrete. In addition to the negative effect of hard paraffins on bitumen during aging, its group composition also changes, that is, the amount of oil in the composition decreases and the tar-asphalt components increase. Secondary alkanolamines were used as modifiers in the experiments in order to prevent wear and destruction of bitumens and to increase their service life. These are used as absorbents in the gas processing industry and are released as waste. Physico-chemical properties of secondary alkanolamines changed due to the absorption of sour gases in the gas composition, that is, the boiling point and viscosity increased, and the freezing point decreased (Table 1).

Table 1. Alkanolamines Physicochemical properties of secondary alkanolamines

Alkanolamine solutions	Concentration		Boiling temperature (180 kPa), °C	Freezing temperature, °C	Viscosity 0°C, 103 Pa*s
	kmol/m ³	%			
IMEA	2.5	65	123	-11	1.6
IDEA	2	71	124	-12	2.0
IMMEDIATELY	2	74	126	-14	2.9

IMEA-used monoethanolamine; IDEA-used diethanolamine; IMDEA-used methyldiethanolamine.

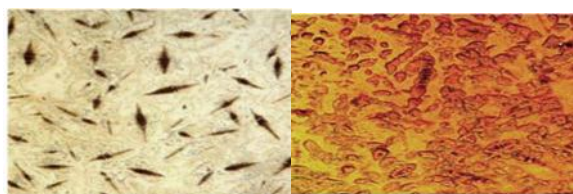
When studying its composition, sour gases in natural gas (H₂S, CO₂, SO and their compounds) and was found to consist of salts. Taking into account the compounds of sour gases contained in secondary alkanolamines, they were studied because they can be used as structuring process accelerators in the polymer-bitumen composition. Before using them, the water content was removed. The effect of alkanolamines on improving the adhesion properties of polymer-bitumen composites, as well as on other physical-mechanical properties of bitumen, was studied. The analysis of the obtained samples showed that industrial waste and used amines had a positive effect not only on increasing the adhesion properties of bitumen, but also on softening and embrittlement, as well as on the depth of penetration of the needle (Table 2).

Table 2. Chemical, physical-mechanical and operational properties of bitumen modified with alkanolamines

Modifier	Modifier concentration, % mass.	Temperature, °C		Penetration, 0.1 mm		Mass loss after heating, % mass.	Softening temperature, °C
		to soften	fragility	25°C	0°C		
IMEA	0	49.5	-11.2	16	70	1.0	8.0
	1	51.5	-8.0	14	57	0.8	7.0
	2	52.0	-8.0	14	57	0.9	7.0
	3	52.5	-11.0	16	51	0.6	6.0
	5	54.0	-13.0	16	40	0.6	6.2
	7	53.5	-6.5	12	50	0.6	6.0
IDEA	1	50.0	-8.3	14	54	0.9	7.5
	2	52.0	-2.7	9	50	0.9	6.8
	3	50.0	-12.2	16	73	0.6	6.0
	5	51.5	-4.3	10	52	0.5	5.5
	7	52.0	-5.0	11	56	0.5	6.5

In general, the use of secondary waste products in improving the chemical, physical-mechanical and operational properties of local bitumen is more profitable from the ecological and economic point of view. In this case, we suggested to add high molecular weight waste to the composition up to 10% of the total volume. In order to reduce the body cost of the composition, waste rubber materials and carbonaceous materials from tire shredding were added.

The clean microrelief of bitumen is sensitive to the additives introduced into it, and the change of the bitumen structure is observed with the change of its properties. For example, the addition of crushed resin and alkanolamine resins to bitumen (2% mass) leads to the formation of microreliefs of a large globular structure. These cases are indicated by elements in elliptical shapes (Fig. 2, b). Under such thermodeformation processing conditions, the initial appearance of the sample (heating at 180 °C for 20 min, then slowly cooling) is characterized by large corrugated and fine-grained globules (Fig. 2, a). Adding this additive changes the technical properties of bitumen as follows: softening temperature increases by 1 °C, penetration at 25 °C decreases from 130 to 83 values, elongation at 25 °C decreases from 68 to 14.3. The obtained results are represented by the structuring effect of the additive.

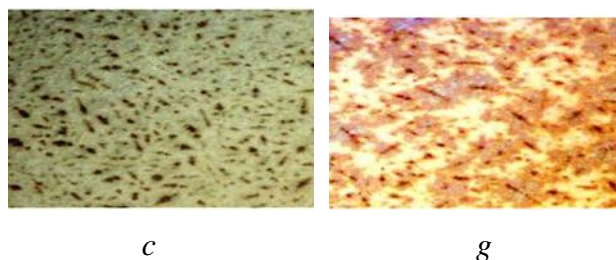
*a**b*

a - initial bitumen; *b* - crushed rubber and alkanolamines
bitumen with added tars (2% mass.);

Figure 2-a,b. Effect of chemical additives on the structure of oxidized bitumen BND 90/130. (Optical microscopy, x200)

BND 90/130 also causes a change in the surface microrelief when lubricating rubber is added to road bitumen. When adding 3-8% mass of crushed rubber, the length of corrugated elements is

reduced by 2 times. At the same time, the size of the globules around the corrugations also increases (Fig. 2, v,g), small grains are formed around the corrugations. The decrease in the corrugation size can be explained by the decrease in the solubility of the dispersion medium in relation to the dispersed phase.



*c and g is bitumen with added carbonaceous material obtained from pulverized rubber
(3 and 8 % by mass.)*

Picture 2 -v,g. Effect of carbonaceous materials on the structure of oxidized bitumen BND 90/130 . (Optical microscopy, x200)

Analysis and conclusions. The analysis and results showed that the formation of these structures leads to an increase in the amount of areas and a decrease in the size of the asphalt-tar structure formations. The change of the structure had its effect on the properties of bitumens. For example, the softening temperature increased from 45 °C to 50 °C when 5% by mass of pulverized rubber carbonaceous material was added to the oxidized BND 90/130 bitumen obtained at the Fergana oil refinery. At 25 °C, penetration and elongation decreased from 95 to 81x0.1 mm and from 70 to 23 cm.

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