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INFLUENCE OF ADDITIVES – OIL TAR MODIFIERS ON THE OXIDIZED BITUMEN ADHESION TO MINERAL MATERIALS

Petroleum tar was exposed to microwave irradiation or added with isopropyl alcohol and then oxidized to paving bitumen. The bitumen adhesion to mineral materials was investigated. Either of the two kinds of treatment enhanced the bitumen adhesion to marble chips and sand. The adhesion to the marble chips ran up to 5 points in contrast to 3 point of the sand adhesion magnitude. Addition of the alcohol to the tar promotes rise in alcohol benzene and benzene resins content in resulting bitumen to the greater extent than the microwave irradiation which leads to reinforcing its bond with marble chips and sand.

Key words: oil tar, additive-modifier, oxidation, bitumen, marble chips, sand, adhesion.

Introduction. Repeated exposure of asphalt pavement rain, snow, sun rays have a significant impact on their quality of adhesion to mineral materials, the ability of bitumen to resist on the surface of mineral materials and, accordingly, the performance properties of road surfaces. Therefore, it is important to consider the quality of adhesion, i.e. adhesive strength of the bitumen to the main content of organic-mineral composite. It is believed [1] that the intensity of adhesion of the bitumen to the surface of the mineral material is determined by the difference in their polarities. The molar polarization of a compound of resins and asphaltenes in the bitumen is determined by the ratio in the system of oil – resins – asphaltenes [2, 3]. Due to intermolecular interactions between closely spaced particles of asphaltenes and resins asphaltene complexes 2.4 and 2.6 nm and associates of these complexes with a size of 9–10 nm are formed. However, at higher temperature intermolecular interactions are weakened, improving the orientation of the dipoles in the bitumen and increases the polarization [3]. I.e. when the formation of complexes of resins and asphaltenes is possible to block the fragments carrying charges. When the temperature changes the structure of the bitumen with the release of polar groups. One of the options to improve the adhesion of the binder to the surface of the mineral material is the modification of bitumen by the use of adhesive additives which enhance the adsorption and chemisorption processes on the interphase boundary “bitumen – mineral material” [4]. As such additives surfactants [5, 6], nitrogen-containing compounds [7], etc., which are introduced into the bitumen in small quantities (up to 1 wt %) are used. However, the main disadvantage of this method is the complexity of uniform distribution of the additive in the volume of high viscosity oil – bitumen.

Main part. In this work, the objective was to investigate the influence on adhesion of oxidized bitumen to mineral materials of additives introduced into the raw material – oil sludge. To assess the adhesion of oxidised bitumen with mineral materials

a standard technique [8] based on maintaining the bitumen covered with mineral material (marble chips, sand) in boiling water with a visual estimate of the surface, which separates the bitumen and comparison with photographs of the control samples was used. If after the test, adhesion of bitumen with mineral material corresponds to the control sample No. 1, i.e. 5 points, according to [1], so a complete covering of bitumen mineral material occurs.

However, the standard method of assessing adhesion of bitumen with mineral material does not allow to quantify the adhesion of the bitumen, therefore, for a rapid assessment of adhesion properties of bitumen is proposed to measure the value of its dielectric constant [9] or to determine the proportion of bitumen remaining on the surface of the mineral material after exposure to the system “bitumen-mineral material” hot water [10, 11]. The objects of study in this work were the samples of bitumen obtained by oxidation of petroleum tar, produced by JSC “Naftan” (Table 1).

Table 1

**The conditions for obtaining samples
of oxidized bitumen**

Sample of bitumen	Temperature oxidation of bitumen, °C	Oxidation time, h	Method of impact on tar
1	245	6	–
2	245	6	Microwave irradiation (60 s)
3	245	6	Microwave irradiation (30 s)
4	245	6	1.5 wt % isopropyl alcohol

Quantitative determination of adhesion of bitumen with mineral material is carried out on the basis of the standard method [10] based on the determination of the mass of the bitumen remaining on the surface of the mineral material after boiling bitumen-mineral mass in the water.

Table 2

Indicators of adhesion of bitumen with mineral material

Sample number	Marble chips				Sand			
	X, %	Δ, %	Number of a control sample	Adhesion in points	X, %	Δ, %	Number of a control sample	Adhesion in points
1	29.16	–	3	3	10.0	–	3	3
2	55.00	88.6	2	4	28.34	183	3	3
3	66.67	129.2	2	4	43.33	333	2	4
4	78.34	168.1	1	5	55.00	450	2	4

The calculation of the index of adhesion (X, %) the quantitative method was carried out according to the following formula:

$$X = \frac{m_i - m}{0.6} \cdot 100, \text{ wt } \%,$$

where m_i is the mass of bitumen-mineral mixture after boiling, g; m – suspension of mineral material, g; 0.6 – hanging bitumen (constant for a given method).

The effects of additives to the tar on the adhesion of the bitumen was determined by the value of the relative difference in adhesion of bitumen with mineral material Δ (%) according to the formula

$$\Delta = \frac{X_a - X_{orig}}{X_{orig}} \cdot 100\%,$$

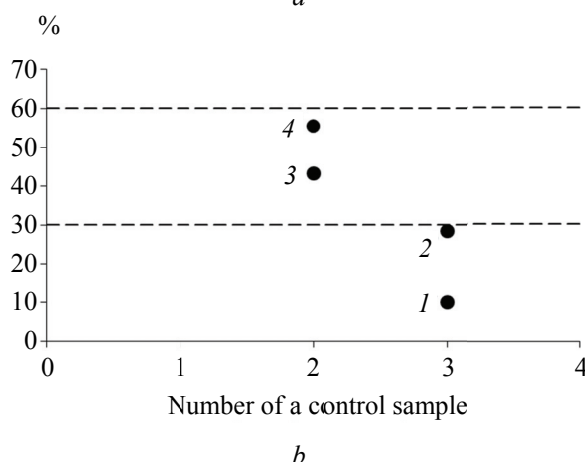
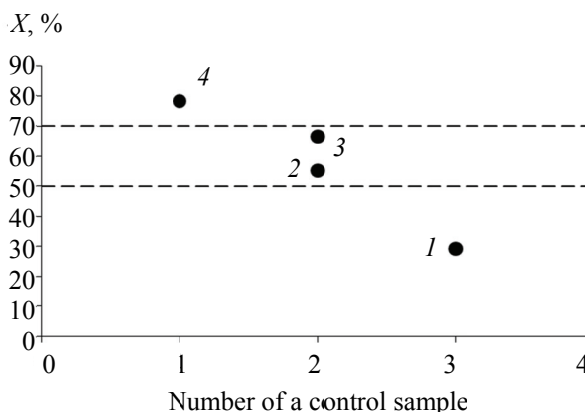
where X_a is the indicator of adhesion of the bitumen derived from tar-containing additives; X_{orig} – adhesion of bitumen obtained from native tar with mineral material.

The results of evaluation of adhesion of bitumen samples by the standard (visual) and quantitative methods are presented in Table 2.

According to [10], when comparing the results of determining the adhesion of the bitumen obtained by the standard (visual) and quantitative methods, we can distinguish the boundaries of the regions quantitative values of adhesion, the respective numbers of the control samples. The figure shows the results of the study of adhesion properties of bitumen by both methods.

According to the figure, when the value of the adhesion with marble chips is above 70% and sand is greater than 50%, bitumen corresponds to samples No. 1 and 2 and will have a good adhesion to mineral material. Bitumen obtained from native tar on the efficiency of adhesion to mineral materials is inferior to oxidized bitumens obtained from tar, subjected to external impact.

The analysis of group composition of bitumens (Table 3) confirms that the adhesion of bitumen with mineral materials significantly influences the relationship between alcohol-benzene resins and asphaltenes.



The relationship between sample number and adhesion: 1, 2, 3, 4 is the number of test sample

Table 3

Group composition of oxidized bitumen

Sample	The relative content			
	Oils	Benzene resins	Alcohol-benzene resins	Asphaltenes
1	17	4	1	9
2	17	4	1	8
3	18	4	1	8
4	13	3	1	5

Apparently, in complex structural unit of the oil dispersion system in the oxidation of native tar and tar subjected to processing of microwave radiation,

the more intense is the seal of the alcohol-benzene resins asphaltenes compared to the rate of formation of polycyclic structures with aliphatic side chains, i.e. benzene resins from components comprising oils, as well as with the speed of formation of the structures of the alcohol-benzene resins.

Conclusion. Thus, a comparative analysis of adhesive properties of road bitumens obtained

from native oil tar and tar oil, subjected to the microwave field and isopropyl alcohol, showed that the introduction of tar isopropyl alcohol has a positive effect on group composition of bitumen, because the ratio of “resin : asphaltenes” is 4 : 5, i.e. more than in the samples of bitumen obtained by oxidation of the native tar (5 : 9) and the sludge treated by microwave radiation (5 : 8).

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