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Influence of Adhesive Additives on the Aging of Oxidized Road Bitumen

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Abstract

This paper presents experimental data on the physicochemical properties of oxidized bitumen produced by the oil refinery plants OJSC TAIF-NK and OJSC Syzran Oil Refinery before and after aging in a thin film in the presence of the developed additive Adgezolin, as well as in the composition with polymer-bituminous binders obtained on the basis of these bitumens. The domestic adhesive additives BP-KSP, Adgezol-6 and imported additive Wetfix (Sweden) were used for comparison. The most significant change (ΔT) in brittleness temperature (5.1 °C) was found in bitumen samples modified with 0.35 mass % Adgezol-6 and 0.5 mass % Wetfix additives, which does not correspond to the methodological document of the road construction industry (ODM 218.2.004–2006). In addition, the study of the qualitative properties of polymer-bitumen binders in comparison with the original bitumen shows that the addition of polymers to the studied bitumen has a positive effect on ΔT of softening after heating; this indicator is within the state standard GOST (not more than 5 °C). The introduction of additives also improves the aging stability of the bitumen: introduction of Adgezolin additive in an amount of 0.8 % causes a significant decrease in ΔT of softening. Comparative analysis of the efficiency with respect to industrially developed domestic and foreign additives allows us to emphasize the high quality of modified bitumen based on Adgezolin additive. Malacometric indicators for evaluating the quality of bitumen modified with the developed Adgezolin additive characterize less severe aging of bitumen binders in comparison with the considered additives, which allows us to recommend it for industrial approval.

Keywords: oxidized bitumen, mineral material, adhesive additives, polymer-bitumen binders, aging

INTRODUCTION

It is known that the quality of bituminous binders has a direct effect on the properties of asphalt concrete, especially on low-temperature characteristics, performance lifetime, corrosion resistance, adhesion, and to a lower extent on the high-temperature characteristics. Understanding of the properties of bitumen and their influence on the qualitative characteristics of asphalt concrete is crucial for the selection of materials for making the layers of asphalt concrete with a long service durability.

In the majority of cases, the durability of asphalt concrete pavement is shorter than the standard value. A decrease in longevity is due to various deformations and destruction: chipping, waving, longitudinal and cross fractures, corrugation, shifts, scaling, potholes, *etc.* All these defects appear as a consequence of weather, climatic and mechanical factors. However, the major factor responsible for the destruction of asphaltic concrete pavement during the performance is bitumen aging.

Asphalt concrete is manufactured by mixing bitumen with stone material at high temperatures (160–170 °C). As a rule, during this process, bitumen interacts with atmospheric oxygen, which causes an increase in fragility and intense aging [1, 2].

Bitumen aging includes all reversible and irreversible changes in its chemical composition and structure, that occur during storage, technological processing, and performance [3–6]. This usually occurs in two phases: technological (mainly) and operational. At the first phase, the scale of changes in bitumen properties depends on three main factors:

1) temperature and duration of heating;

2) the ratio of the volume of heated bitumen mass to its free surface;

3) bitumen kind (its viscosity, initial raw material, and method of preparation).

The second phase includes bitumen aging during the operation of the Asphalt concrete pavement [3]. The major factors that cause bitumen aging during operation are:

1) interaction of bitumen components with atmospheric oxygen and water;

2) temperature effect;

3) the effect of the surfaces of mineral materials, the salts of metals with variable valence and organometallic compounds in bitumen;

4) effect of infrared and ultraviolet radiation;

5) mechanical load.

Bitumen aging also includes evaporation. In this process, bitumen loses readily volatile components, chemical transformations of bitumen components take place, which is accompanied by the formation of free radicals and dehydropolycondensation processes [7, 8].

It was revealed that the result of bitumen aging is a change of its composition, which is accompanied by an increase in viscosity, a decrease in plasticity and an increase in fragility [8].

The most intense change of bitumen properties occurs at the phase of technological aging. Long-term heating of bitumen to high temperatures during the preparation of asphalt concrete mixture leads to significant changes in its composition and is accompanied by the loss of binding properties of bitumen and a significant deterioration of these properties [9].

The actual standards GOST 22245–90 and GOST R 52056–2003 for road bitumen and polymeric bitumen binders (PBB) contain, among the recorded parameters, only one providing indirect characterization of the longevity of bitumen binder: change of the temperature (ΔT) of softening after heating for 5 h at a temperature of 163 °C. Thermal aging of bitumen may be represented as two components: 1) thermal distillation – evaporation of light fractions from bitumen under the action of high temperature, which leads to an increase in the concentration of heavy components and to increase in fragility; 2) thermal oxidation, proceeding mainly according to the radical mechanism. It is known that a disadvantage of some types of surface-active substances used as adhesive additives is their low thermal stability [10, 11].

The goal of the work was to study the effect of adhesive additives on the aging resistance of bitumen and to make a comparative evaluation of the effect of commercially available adhesion additives on the temperature-induced degradation of the modified binder.

EXPERIMENTAL

Materials used in the investigation included:

– crushed stone from the Pervouralsk deposit (diorite, the Sverdlovsk Region) and the Biyanka Crushed Stone Plant (carbonate, the Chelyabinsk Region), fraction 20–40 mm;

– oxidized bitumen of BND 60/90 grades, produced at the oil refinery plants (ORP) OJSC TAIF-NK (the Republic of Tatarstan) and OJSC Syzran Oil Refinery;

– additives: Adgezolin (Kazan, Russia), Adgezol-6 (Kazan, Russia), BP-KSP (Ufa, Russia) and Wetfix (Sweden)[12–14];

– polymeric bitumen binders (PBB) based on bitumen BND 60/90 from OJSC TAIF-NK and OJSC Syzran Oil Refinery, and synthetic ethylene propylene dienic caoutchouc (SCEPD) SCEPD with dicyclopentadiene (DCPD) [15].

The additives were introduced into bitumen in optimal doses recommended by the developers, mass %: BP-KSP 0.8, Wetfix 0.5, Adgezolin 0.8, Adgezol-6 0.35.

Evaluation of the adhesion of bitumen binder to the mineral material was carried out according to GOST 11508–76 using method A (so-called passive adhesion), the essence of which is determining the ability of viscous bitumen to stay on the surface of mineral material under the action of water [16].

Visual examination of the surface of crushed stones to determine the degree of bitumen film conservation was used to evaluate its adhesion to the surface of the mineral material. A five-score system was used to evaluate the quality of adhesion of the bitumen binder [17]. Bitumen is considered to pass the test for passive adhesion if after the test its adhesion to the mineral material corresponds to the reference sample No. 1 (or the score of 5), that is, a continuous coating of the surface of stone material with bitumen is observed.

According to the standard test method ASTM D2872–2004 (the RTFOT method) [18], the samples of oxidized bitumen produced by OJSC TAIF-NK, modified with different additives, were tested for aging in thin film using Matest instrument (Italy). The instrument is a furnace for bitumen aging with electric heating. The furnace should be equipped with a rotating cylinder 300±10 mm in diameter, composed of three aluminium discs fixed on a common axis and connected with each other through screw bolts and disjunctive plugs (front and rear). The discs separated by the front plugs should have eight orifices each for glass containers that are filled with bitumen. During the test, the furnace should have an internal temperature of 163±1 °C inside. The test temperature is reached within less than 15 minutes after the samples are mounted. The empty glass containers that are used to determine the changes in sample mass should be marked and weighted with the accuracy of 1 mg. Each glass container is filled with 35.0±0.5 g of the sample. Immediately after pouring the bitumen samples, the bitumen must be distributed on the inner side surface of the container by rotating the glass container. Then the containers with bitumen must be cooled for not less than 1 hour at a temperature of 21±4 °C. After that, they are weighted with an accuracy of up to 1 mg. Then it is necessary to switch on the rotation of the cylinder, at a frequency of 15.0±0.2 min^{-1}, to supply air flow at a rate of 4.0±0.2 L/min through a pulverizer, and to start test timing. The glass containers with the samples are to be kept under these conditions in the furnace for the time necessary for the test (85±1 min). After that time, the containers are to be taken out of the furnace and to be placed for cooling at a temperature of 21±4 °C for not less than 1 hour. Then the glass containers are weighted with an accuracy of up to 1 mg. Taking all containers out in turn, it is necessary to collect bitumen from the containers into one vessel, transferring not less than 90 % of bitumen from each container into this vessel [19]. Then the required tests are carried out.

According to the methodological document of the road construction industry ODM 218.2.004–2006 Recommendations for the determination of stability against aging and viscosity of bitumen [20], it is recommended to determine the stability of bitumen samples against aging on the basis of: ΔT of softening, residual penetration at 25 °C (RP, %), changes of the absolute values of fragility temperature and the change of penetration index (PI).

It is considered unreasonable to determine some parameters of bitumen after heating: penetration at 0 °C, and ductility at 25 and 0 °C. For bitumen, ductility at 25 °C is often higher than 100 cm, while at 0 °C fragile rupture occurs (a sample is cleaved under a minimal stretching force). The change of penetration parameter at 0 °C after bitumen heating gives valuable information to evaluate the stability of bitumen to aging, but the inclusion of this parameter into evaluation would cause a substantial increase in labour intensity of the entire set of tests because it would be necessary to use much more glass vessels with bitumen [20].

Residual penetration (RP, %) at 25 °C was calculated using the equation:

$$RP = \frac{P_1}{P} \cdot 100\ \%$$

where P and P_1 are penetrations of bitumen (0.1 mm) before and after heating, respectively.

The change of bitumen fragility temperature after heating was determined as the difference of the absolute values of fragility temperature before and after the heating test. The change of PI of bitumen after heating is calculated as the difference of the absolute values of PI before and after the bitumen heating test.

RESULTS AND DISCUSSION

It can be seen from the data presented in Table 1 that the additive Adgezolin has a positive effect on the softening temperature, compared to the commercial additives with comparable values and complies with the requirements of GOST. The worst ΔT of softening is observed for initial bitumen and corresponds to 9.1 °C. It should also be emphasized that the highest ΔT of fragility (5.1 °C) is observed for bitumen modified by additives: 0.35 mass % Adgezol-6 and 0.5 mass % Wetfix (Fig. 1).

TABLE 1

Physicochemical characteristics of oxidized bitumen produced at OJSC TAIF-NK

Parameter	GOST 22245–90	Bitumen sample											
		Before aging						After aging					
		Initial	+ 0.8 % Adgezolin	+ 1.0 % Adgezolin	+ 0.5 % Wetfix	+ 0.35 % Adgezol-6	+ 0.8 % BP-KSP	Initial	+ 0.8 % Adgezolin	+ 1.0 % Adgezolin	+ 0.5 % Wetfix	+ 0.35 % Adgezol-6	+ 0.8 % BP-KSP
Penetration, 0.1 mm: at 25 °C	Not less than 61–90	58	61	64	94	56	55	27	28	29	26	29	29
Softening temperature R&B[a], °C	Not lower than 47	47.5	48.7	48	50	48.7	47.1	58.6	56.4	55.8	59.6	57.2	57.0
Adhesion to crushed stone, score:	Not standartizied												
Pervouralsk		2	5	5	5	5	5	2	4	5	5	3	3
Biyanka		3	5	5	4	4	5	2	5	5	4	3	3
Penetration index	From −1 to +1	−1.5	−1.1	−1.1	0.5	−1.3	−1.7	−0.6	−1.0	−1.0	−0.5	−0.7	−0.8
Fragility temperature, °C	Not higher than −15	−20.2	−23.8	−26.3	−23.3	−22.3	−22.9	−16.2	−20.2	−23.2	−17.7	−16.7	−18.7
Change of softening temperature after heating, °C	Not more than 5	–	–	–	–	–	–	9.1	4.8	4.7	6.6	6.5	6.9
Residual penetration at 25 °C, %	Not less than 46	–	–	–	–	–	–	47	46	46	28	52	53
Change of fragility temperature, °C	Not more than 3	–	–	–	–	–	–	3.5	3.0	3.0	5.1	5.1	3.7
Change of penetration index	Not more than 0.7	–	–	–	–	–	–	0.9	0.1	0.1	1.0	0.6	0.9

Note. Dash means the absence of data.

[a] Ring and ball method.

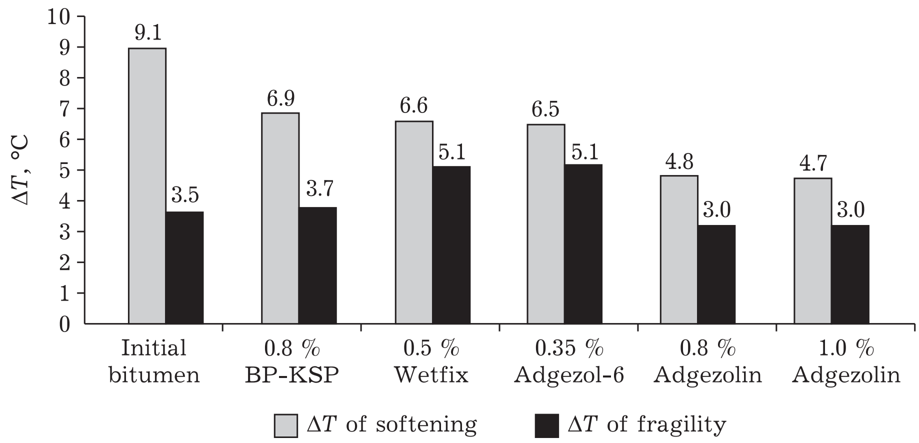

Fig. 1. Changes of the temperature (ΔT) of softening and fragility after heating the samples of initial bitumen (OJSC TAIF-NK) and bitumen modified with additives.

For all bitumen samples, RP corresponds to ODM 218.2.004–2006, except bitumen sample modified by 0.5 mass % Wetfix (RP 28 %). With respect to PI change, the samples of initial bitumen and bitumen samples modified with BP-KSP and Wetfix additives did not correspond to the requirements of the standard ODM 218.2.004–2006 (the changes of PI were 1.0 and 0.9, while the required value was not more than 0.7, see Table 1).

The trend to develop PBB compositions and to apply them in road pavement is observed worldwide, so we considered the efficiency of the additive within PBB. We used PBB obtained by us under laboratory conditions on the basis of initial oxidized bitumen samples from OJSC TAIF-NK and OJSC Syzran Oil Refinery (Table 2). We also studied PBB with adhesive additives: with the addition of 0.8 mass % Adgezolin and 0.35 mass % Adgezol-6. Results of the investigation of the qualitative characteristics of PBB are presented in Table 3.

Comparative analysis of the qualitative characteristics of PBB and initial bitumen revealed the following: the addition of polymers into the bitumen samples under investigation had a positive effect on ΔT of softening after heating; that is, this parameter is within the GOST requirement (not more than 5 °C). The introduction of additives also causes an increase in the stability of bitumen against aging: the introduction of 0.8 % of Adgezolin additive causes a noticeable decrease in ΔT of softening. The addition of 0.35 % of Adgezol-6 causes a definite increase in this parameter, which has a negative effect on the properties of the binder and, consequently leads to increased brittleness, with premature wear of the road pavement (Fig. 2).

Residual penetration and the change of PI for all bitumen samples correspond to ODM 218.2.004–2006, except for the sample of initial bitumen produced at OJSC Syzran Oil Refinery (PI changes by 1.2). In general, all other samples correspond to ODM 218.2.004–2006.

CONCLUSION

Thus, the reported results show that the developed additive Adgezolin has an increased adhesion to the surface of mineral materials. A distinctive feature of Adgezolin additive in comparison with some local and foreign analogues is the technological expediendcy of its application (compatibility with bitumen at relatively low temperature, 120–130 °C), high thermal stability, the absence of specific odour, the relative cheapness of the product.

As a result of the studies of the effect of Adgezolin additive on the properties of a number of bitumen samples and comparative analysis of its effectiveness with involving commercially available local and foreign additives, it is necessary to stress the high quality of bitumen modified with the developed adhesive additive. The considered parameters of bitumen quality (changes of softening and fragility temperatures, change of penetration index and residual penetration), which in many respects characterize the degree of bitumen aging, allow us to evaluate the developed additive Adgezolin as a modifier that promotes less intensive aging of bitumen binders in comparison with other considered additives, which enables us to recommend it for industrial approval.

TABLE 2

Physicochemical characteristics of oxidized bitumen produced at OJSC TAIF-NK and OJSC Syzran Oil Refinery, and PBB based on these bitumen samples

Parameter	GOST 22245–90	Bitumen samples							
		Before aging				After aging			
		TAIF-NK	Syzran Oil Refinery	PBB TAIF-NK	PBB Syzran Oil Refinery	TAIF-NK	Syzran Oil Refinery	PBB TAIF-NK	PBB Syzran Oil Refinery
Penetration, 0.1 mm: at 25 °C	Not less than 61–90	58	47	66	69	27	38	51	57
Softening temperature, R&B, °C	Not lower than 47	47.5	49.6	69.2	69.2	58.6	57.2	74.1	72.9
Adhesion on crushed stone, score:	Not standardized								
Pervouralsk		2	2	2	2	2	2	2	2
Biyanka		3	3	3	3	2	3	3	3
Penetration index	From −1 to +1	−1.5	−1.4	3.5	3.6	−0.6	−0.2	3.5	3.7
Fragility temperature, °C	Not higher than −15	−20.2	−22.6	−42.0	−34.3	−16.2	−19.3	−28.6	−27.8
Change of softening temperature after heating, °C	Not more than 5	–	–	–	–	9.1	7.6	4.9	3.7
Residual penetration at 25 °C, %	Not less than 46	–	–	–	–	47	81	77	83
Change of fragility temperature, °C	Not more than 3	–	–	–	–	3.5	5.3	8.4	6.5
Change of penetration index	Not more than 0.7	–	–	–	–	0.9	1.2	0	0.1

Note. Here and in Table 3: 1. PBB – polymer bitumen binder. 2. Residual penetration at 25 °C, change of fragility temperature, and change of penetration index were evaluated for agreement with ODM 218.2.004–2006. 3. Dash means the absence of data.

TABLE 3

Physicochemical characteristics of PBB with adhesive additives

Parameter	GOST 22245−90	PBB sample with additive							
		Before aging				After aging			
		TAIF-NK + 0.8 % Adgezolin	Syzran Oil Refinery + 0.8 % Adgezolin	TAIF-NK + 0.35 % Adgezol-6	Syzran Oil Refinery + 0.35 % Adgezol-6	TAIF-NK + 0.8 % Adgezolin	Syzran Oil Refinery + 0.8 % Adgezolin	TAIF-NK + 0.35 % Adgezol-6	Syzran Oil Refinery + 0.35 % Adgezol-6
Penetration, 0.1 mm: at 25 °C	Not less than 61−90	58	64	53	62	43	48	41	46
Softening temperature, R&B, °C	Not lower than 47	67.4	63.3	66.5	67.1	71.3	66.7	74.9	73.3
Adhesion to crushed stone, score	Not standardized								
Pervouralsk		5	5	5	4	5	4	5	3
Biyanka		5	5	5	5	5	5	5	4
Penetration index	From −1 to +1	2.8	2.3	2.4	2.7	2.7	2.2	3.1	3.1
Fragility temperature, °C	Not higher than −15	−38.5	−46.0	−38.4	−45.0	−33.3	−30.8	−31.4	−24.0
Change of softening temperature after heating, °C	Not more than 5	–	–	–	–	3.5	3.4	8.4	6.2
Residual penetration at 25 °C, %	Not less than 46	–	–	–	–	74	75	77	74
Change of fragility temperature, °C	3	–	–	–	–	5.2	6.2	7.0	8.0
Change of penetration index	Not more than 0.7	–	–	–	–	0.1	0.1	0.7	0.4

Note. For designations, see Table 2.

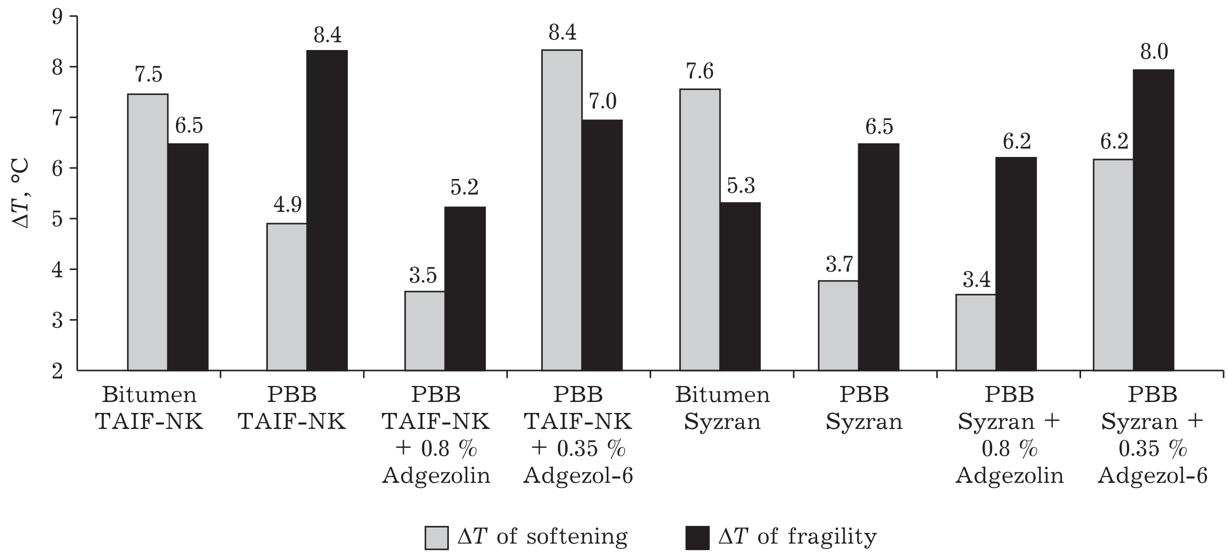

Fig. 2. Changes of the temperature (ΔT) of softening and fragility after heating the samples of initial bitumen and polymer bitumen binders (PBB) with additives.

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